Quality Control Sampling

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Outline

- Quality Assurance/Quality Control
- Quality Control Sample Types
- Quality Control Sample Design

Design of Samples

- Decide what information the analysis of the samples will provide.
- Decide how you will use that information.
- QC information will be an integral part of achieving the study objectives.
- Good QC sample design depends on good environmental sample design.
- Put aside ideas that QC samples should be some percent of the environmental samples.

Variable Scale Projects

SMALL PROJECT

- Single site
- One set of equipment
- One sampling team

LARGE PROJECT

- Multiple sites
- Multiple sets of equipment
- Multiple sampling teams

Facets of Quality Assurance

- Quality Assurance Elements
- Quality Control Data
- Quality Assessment

Quality Assurance

- Procedures used to control those unmeasurable components of a project, such as sampling at the right place with the right equipment and using the right techniques.

Quality Control

- Data generated to estimate the magnitude of the bias and variability in the processes for obtaining environmental data.

Quality Assessment

- Overall process of assessing the quality of the environmental data by reviewing the application of the QA elements and the analysis of the QC data.

Example Data Problem

- Trace metals:
  - For years trace metal samples were contaminated from sample collection and processing.
  - Field blanks would have shown the presence of contamination and been instrumental in interpreting the data.
  - Led to the clean hands / dirty hands ppb protocol that everyone uses now.

Example Data Problem

- Ammonia:
  - Positive bias 1979-1982 from HgCl2 tablets used to preserve nutrient samples.
  - Found with comparison of data from Denver to data from Atlanta lab (Atlanta did not use the tablets). Subsequently detected with trend analysis.
  - Field blanks or lab blanks would have identified the presence of a bias. Further investigation would have been needed to identify the source.
  - Now have a blind blank program for inorganic methods at NWQL.

QC Information

- The data from QC samples measure errors in the environmental data.
- We can measure two types of errors with the QC samples:
  - ✓Bias
  - ✓Variability

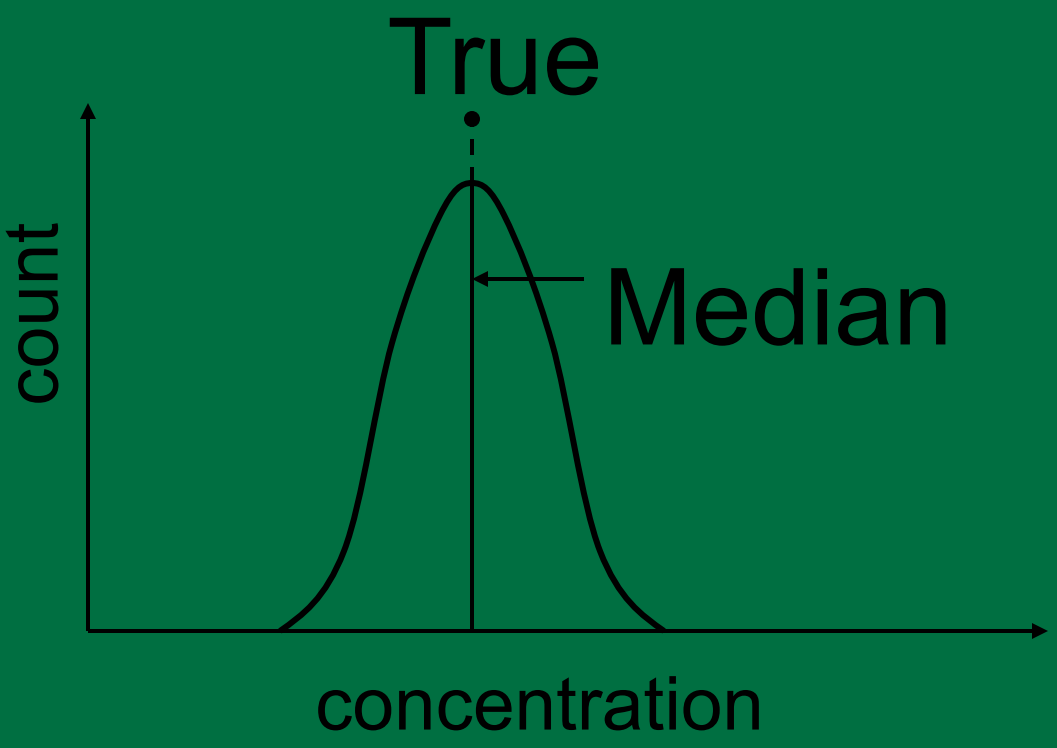
Bias

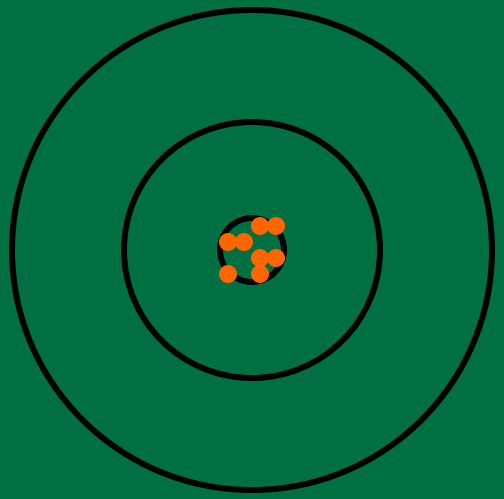
- Systematic error inherent in a method or measurement system. The error can be positive (contamination) or negative (loss).

Variability

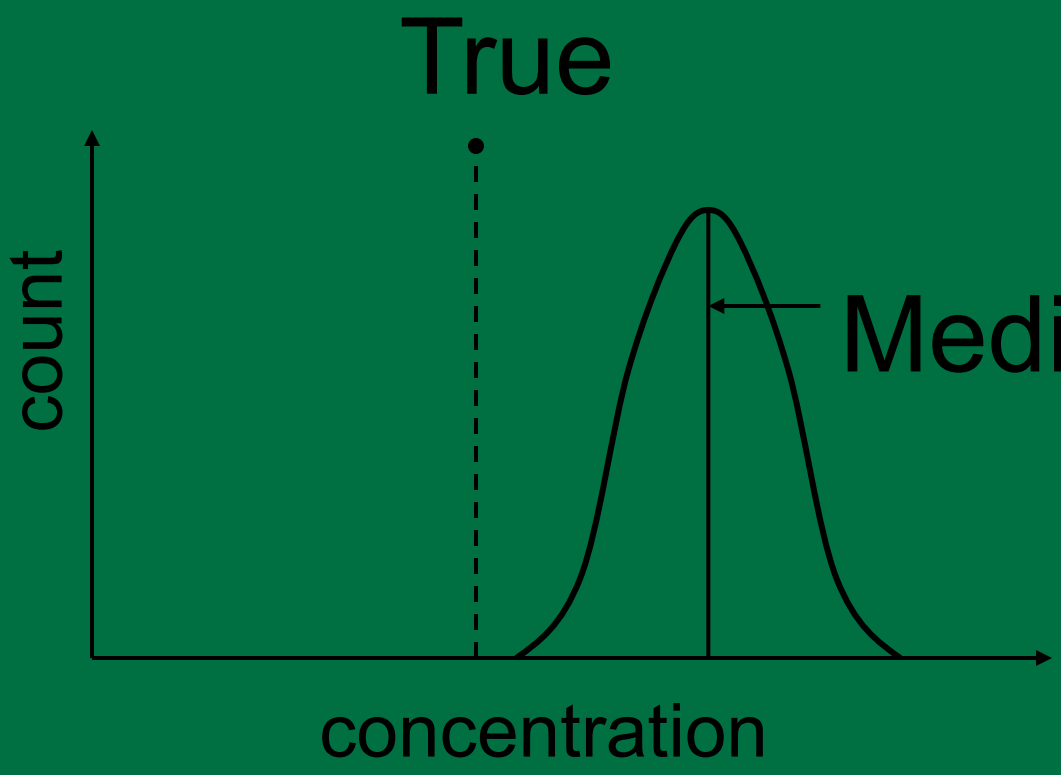
- Random error in independent measurements as the result of repeated application of the process under specific conditions.

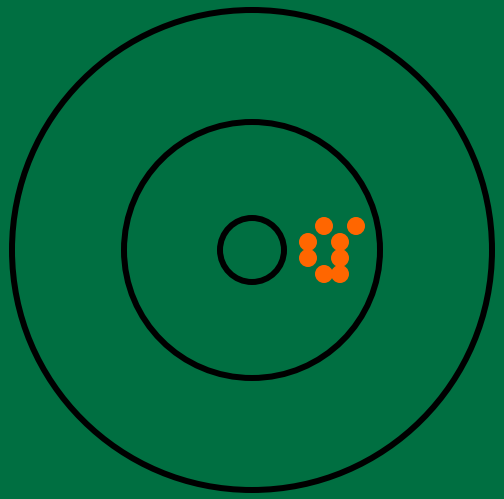
Low Bias & Low Variability



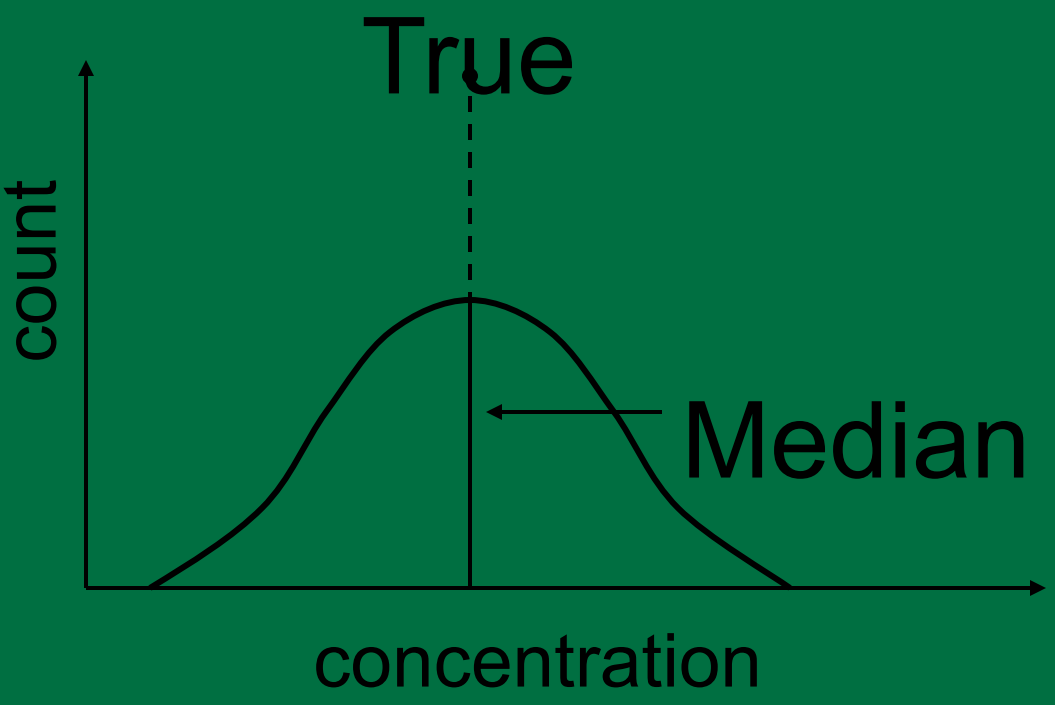


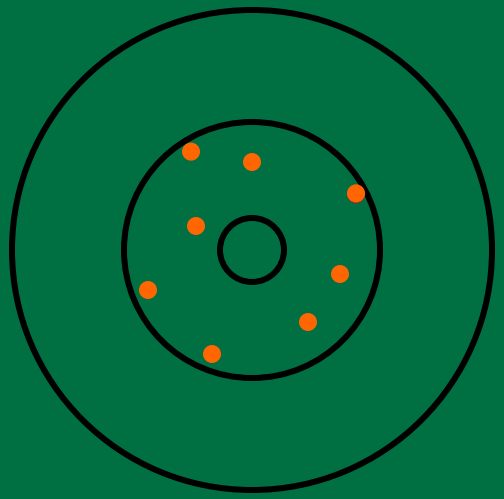
High Bias & Low Variability



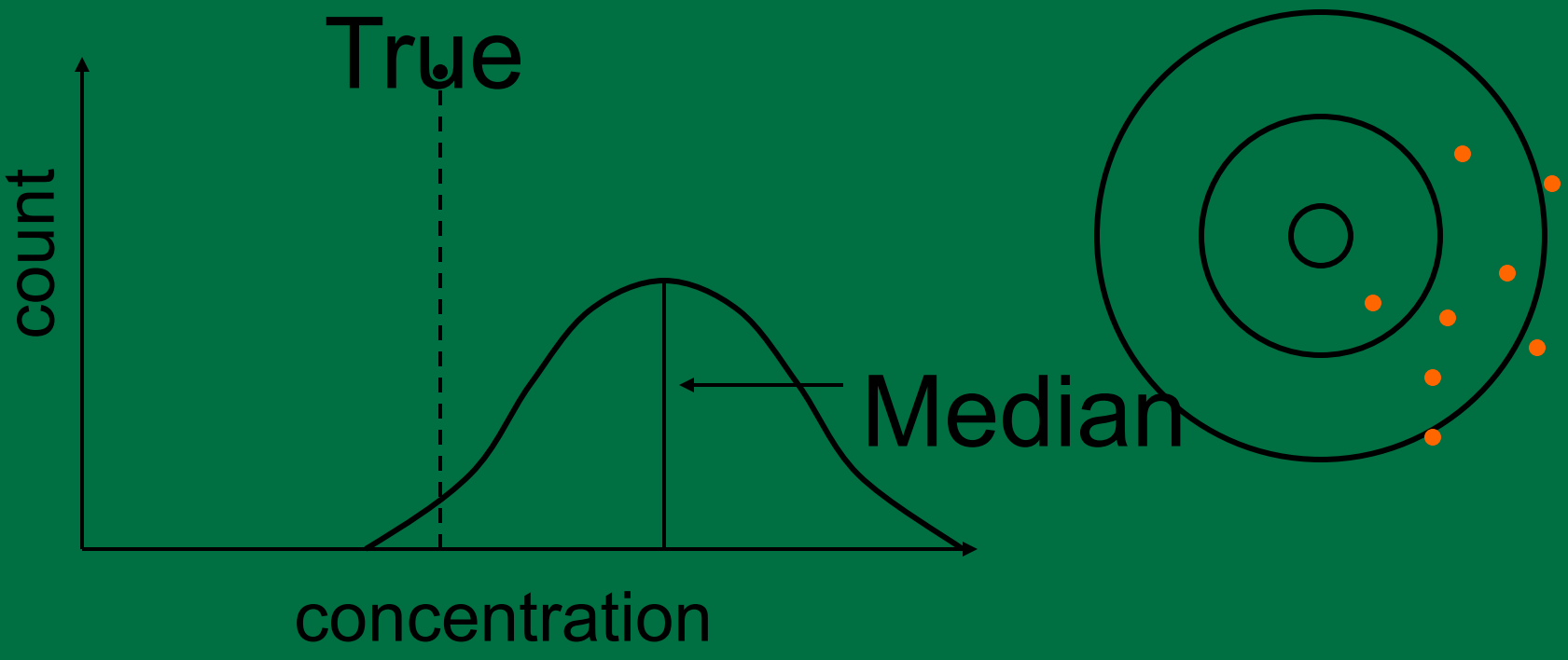


Low Bias & High Variability





High Bias & High Variability



Other Common Terms

- Accuracy: The degree of agreement of a measured value with the true or expected value of the quantity of concern.
- Precision: The degree of mutual agreement characteristic of independent measurements as a repeated application of the process under specific conditions.


SPEED BUMP
ON SECOND THOUGHT, MAYBE I'LL JUST DO SOME SIGHTSEEING...
BUSINESS CONFERENCE
QALITY CONTROL SEMINAR

Quality Control Sample *TYPES*

U.S. Department of the Interior
U.S. Geological Survey

Overview

- Introduction to 4 general QC sample types
- Objectives of QC samples
- Important difference between “Basic” and “Topical” QC samples
- Discussion of QC sample “sub-types” and what they do and do not measure
- My opinions / recommendations

QC Samples Estimate Errors

- Bias
  - Blanks
  - Spikes
  - Reference Materials
- Variability
  - Replicates
  - Spikes (for selected concentrations)
  - Reference Materials (for selected concentrations)

Blanks

- Definition
  - Samples prepared with a special type of water (or other media) that is certified to be free of the analytes that will be measured by a laboratory
- Purpose
  - Used to test for bias from the introduction of contamination into environmental samples

Replicates

- Definition
  - Two or more samples that are considered to be essentially identical in composition
- Purpose
  - Used to estimate variability for all or some part of the measurement process

Reference Samples

- Definition
  - Samples containing certified concentrations of analytes that will be measured by the laboratory
- Purpose
  - Used to evaluate the bias of an analytical method

Spikes

- Definition
  - Samples fortified with known concentrations of specific analytes that will be measured by the laboratory
- Purpose
  - Test for bias from the analytical method, or matrix interference, or degradation

QC Sample Objectives

- Estimate the bias and variability of the environmental data
- Enable compensation for bias in data analysis.
- Allow for qualification of interpretations or conclusions
- Locate (if needed) causes of data-quality problems.

Classification of QC Samples by the Intended Use of the Information

- BASIC vs. TOPICAL

  If you remember one thing from this section, this is it !!!

Basic QC Samples

- BASIC QC samples are used to:
  - Estimate the bias and variability of the environmental data
  - Identify data-quality problems. Do I have a problem or not? Problems identified by comparing QC results to environmental data or to expectations of data quality

Basic QC Samples

- BASIC QC samples measure all or nearly all of the sources of error that affect environmental samples

- Only three types of BASIC QC samples:
  - Field Blanks
  - Field Matrix Spikes
  - Field Replicates

Topical QC Samples

- TOPICAL QC samples are used to:
  - Locate the cause of data-quality problems
  - Assess “comparability” of methods
  - Make a yes / no decision to initiate sampling
  - Verify that blank water is suitable for use

Topical QC Samples

- TOPICAL QC samples measure a limited number of sources of error that affect environmental samples
- TOPICAL QC samples are intended to measure some specific aspect of bias or variability
- Many types of TOPICAL QC samples (anything other than field blanks, field matrix spikes, and field replicates)

Questions?

Some Types of Blanks

Type	Targeted Source of Bias	Use
Field	All -- Sample collection, processing, transport, field environment	Basic
Equipment	Sample collection and processing equipment	Topical
Sampler	Sampler. For example: D-95 or Fultz pump	Topical
Trip	Transport and storage of empty sample bottles and collected samples	Topical
Ambient	Atmosphere	Topical
Source Solution	Water used to make the blank (Is it clean?)	Topical
Lab	Lab processing and analysis	Topical

Various Types of Blanks and the Sources of Contamination They (Probably) Measure
[T, a tageted source; x, an unavoidable source]

Source/Cause	Basic QC	Topical QC					
	Field	Equip	Sampler	Trip	Ambient	Source	Lab
Field Sources:							
Field environment:							
Air, rain, dust, fumes	T			T	T	x	
Sample collection:							
Samplers	T	T	T				
Sample processing:							
Splitters/filters	T	T					
Sample bottles	T	T	x		x	x	
Water used for the blank	x	x	x	x	x	T	
Cleaning:							
Soap/Carryover	T	T	x				
Transport to/from field:							
Field vehicles/Coolers	T			T	x	x	
Storage:							
Warehouse/Field vehicles	T	x	x	T			
Shipping to lab:							
Coolers	T	x	x	T	x	x	
Personnel:							
Dirty hands/sweat/sunscreen	T	x	x		x	x	
Laboratory Sources:							
Lab environment/Analysis	T	x	x	x	x	x	T

Don’t Rely on Sample Names!

- Think about the sources of error your QC sample is / is not measuring
- **HOW** the QC sample was collected makes all the difference in the sources of error measured by a QC sample

Field Blank Collected Before Sample vs. After Sample

Before:

1. Arrive onsite
2. Collect blank
3. Collect sample
4. Clean equipment
5. Leave site

After:

1. Arrive onsite
2. Collect sample
3. Clean equipment
4. Collect blank
5. Leave site

Potential sources of contamination for this example:
Field environment, field teams, equipment, supplies, inadequate cleaning of equipment, transport of equipment or supplies from office to field, transport equipment, supplies, or samples from field to office, shipment samples to lab.

Ammonia Blanks

Analyte	Blank Type	N	Hits	% Hits	MRL	Med	Max
Ammonia	Field	24	15	62	0.01	0.01	0.07

- Field Blank measures ALL sources of bias
- Do I have a data-quality problem?
- What (if anything) should I do?

Ammonia Blanks - 2

Analyte	Blank Type	N	Hits	% Hits	MRL	Med	Max
Ammonia	Field	24	15	62	0.01	0.01	0.07
Ammonia	Source Solution	14	9	71	0.01	0.015	0.03

- Source Solution Blanks are intended to measure ammonia in the water used to make the blank
- What are the possible sources of contamination in the Field Blank?
- What has been ruled out as possible sources?

Ammonia Blanks - 3

Analyte	Blank Type	N	Hits	% Hits	MRL	Med	Max
Ammonia	Field	24	15	62	0.01	0.01	0.07
Ammonia	Source Solution	14	9	71	0.01	0.015	0.03
Ammonia	Laboratory	51	26	51	0.01	0.01	0.028

- Lab Blanks measure contamination in the analytical method
- What is the probable source of contamination in the Field Blanks?
- Did I waste a bunch of money?

Ammonia Blanks Conclusion

- LESSON:
  - Limit assumptions
  - Communicate and work with others to determine if you have a data-quality problem, and if you do, whether it needs to be located or fixed

Comments on Blanks

- All blanks measure more than one potential source of contamination
- You must use several types of blanks in combinations in order to locate the source of contamination
- Expensive to locate problems

Comments on Blank Water

Use the **appropriate** type / grade of water:

- Inorganic (Nutrients, Ions, Trace Elements, Suspended Sediment)
- Organic (Pesticides and DOC)
- Organic-N2 purged (VOCs, Pesticides, DOC)
- Buffered water (Microbiological analyses)

Comments on Blank Water - 2

- Locally procured or produced blank water must be quality assured by the user
- You may think you are saving money but are you? (Consider the cost of one pesticide or VOC analysis)
- For USGS - Recommend using “official” USGS blank waters from NWQL

Comments on Blank Water - 3

- Inorganic blank water may contain organics and organic blank water may contain inorganics
- Potential for cross contamination if both types of water are used at same site visit
- Recommend only one type of water per site visit

Warning! Not All Blanks Measure Contamination!

- A procedure “blank” for E. coli is buffer water processed through bacteria filtration equipment following filtration of the environmental sample, but before cleaning and sterilizing the filtration equipment
- What sources of error do procedure blanks measure?

Questions on Blanks?

Replicates

- Replicates are “essentially identical” samples. Essentially identical means that the samples are collected, processed, transported, and analyzed the same way
- Replicates measure variability (random error in measurements of the same quantity)

Replicates

- Replicate is the general term. Duplicates are 2 replicates, triplicates are 3 replicates, and so forth

How Field Replicates Are Made

- SPLIT replicates: A single sample that is subdivided into other samples
- CONCURRENT replicates: Multiple samples that are collected at the same time
- SEQUENTIAL replicates: Multiple samples that are collected one after another

Types of Field Replicates

Type	Targeted Source of Var.	Use
Concurrent	All – Sample collection, processing, and analysis	Basic
Sequential	All – Sample collection, processing, and analysis[1]	Basic
Split	Sample processing, analysis (NOT collection)	Topical

[1] Also includes an unknown amount of variability caused by short-term changes in the environment.

Various Types of Replicates and the Sources of Variability They Measure

[T, a targeted source; x, an unavoidable source]

Source/Cause	Basic QC			
	Sequential*	Concurrent		Split*
	Crews	Crews		Crews
	One	One	Two	One
Field Sources:				
Field environment:				
Temporal change in medium	x			
Sample collection:				
Sample collection	T	T	T	
Personal technique			T	
Similar sampling equipment			T	
Sample processing:				
Sample splitting/filtering	T	T	T	T
Personal technique			T	
Similar processing equipment			T	
Other sources (for example):				
Shipping reps same cooler				
Shipping reps similar coolers	T	T	T	T
Laboratory Sources:				
Laboratory environment/Analysis	T	T	T	T

* = Generally NOT done by two crews.

What Is Being Measured?

- Suppose I collect two samples 5 minutes apart. Are my samples Sequential Field Replicates or short-time-interval environmental samples?
- The answer depends on why you are collecting the samples (the use of the data):
  - If it is: To estimate variability, they are replicates.
  - If it is: To investigate temporal changes in water quality, then they are short-time-interval environmental samples (but you still must have an estimate of variability to interpret the significance of differences between short-time-interval environmental samples).

Which Kind of Basic Field Replicates To Collect?

- Technical factors: Some constituents, equipment, or hydrologic conditions not amenable to some types of replicates
  - Can't split VOCs or DO. Can't easily split GW
  - Sequential Reps not appropriate where QW is changing rapidly or in situations where the first replicate may affect second replicate (fish shocking, streambed sampling)
- Logistic or budgetary factors: Costs in time and money
- MY ANSWER: Concurrent field replicates by 1 crew

Comments on Replicates

- Replicates are especially important for interpreting a small number of environmental samples
- The process of collecting replicates may change your “normal” field procedure. Ideally, other factors that could affect variability also should be the same (volumes, times, equipment, personnel, etc.)

Comments on Replicates - 2

- Any “essentially identical” samples can potentially be used as “replicates” to assess variability
  - Multiple samples of the same reference material
  - Multiple spikes in the same matrix
- The key is that they are measured the exact same way (concentration, matrix, method, laboratory)

Comments on Replicates - 3

- Stick with one type of field replicate to measure variability
- Estimates of variability probably are “best case” (true variability probably greater than that measured by replicates) because replicates often are analyzed in the same analytical “set.”

Warning! Not All "Replicates" Measure Variability!

- IRREPLICATES are "essentially identical" samples that are used to investigate some change in the data generation process
- IRREPLICATES are used to assess "comparability" of methods, often to support pooling data
- Comparability usually limited to assessment of difference in bias (not in variability)

Examples of Irreplicates

- Compare analyses by different labs (NWQL vs. COOP)
- Compare analyses by different methods
- Compare preserved vs. not preserved
- Compare filtered vs. unfiltered alkalinity
- Compare suspended-sediment sample from cone splitter with conventionally collected sediment sample
- Compare auto sampler with traditional sampling method
- Compare effect of exceeding holding times

Questions on Replicates?

Spikes

- Spikes measure the bias of the analytical method in a particular matrix
- Bias for spikes is termed “RECOVERY” (the amount measured expressed as a percentage of the amount spiked)

Spikes

- Location spike mixture added
  - In the field
  - In the laboratory
- Matrix
  - in an environmental water sample (a matrix spike)
  - in blank water (a reagent spike)

Reagent Spikes

- Measure the performance (bias) of the analytical method in a “clean” matrix
- Labs do a lot of these to measure performance (control charts)
- Because labs do a lot of them (and in the same water and at the same concentration), lab reagent spikes also measure variability of performance

Matrix Spikes

- Measure the performance (bias) of the analytical method in a real water sample of interest (your water)
- The objective for matrix spikes is to determine if the analytical method performs the same in your real water as it does in blank water
- If different performance, perhaps you have MATRIX EFFECTS or DEGRADATION

Matrix Effects or Degradation

- MATRIX EFFECTS: Some characteristic of the water sample that interferes with analysis
- DEGRADATION: The loss or chemical conversion of the target analyte

Types of Spikes

Type	Targeted Source of Bias	Use
Field Matrix Spike	All -- Matrix effects, degradation, and method performance	Basic
Lab Matrix Spike	Matrix effects	Topical
Field Reagent Spike	Degradation	Topical
Lab Reagent Spike	Method performance	Topical

- FIELD: Spike solution added in field or office
- LAB : Spike solution added in laboratory
- MATRIX: Real water sample
- REAGENT: Blank water sample

Various Types of Spikes and the Sources of Bias They Measure

[T, a targeted source; x, an unavoidable source]

Source/Cause	Basic QC	Topical QC		
	Field Matrix Spike	Lab Matrix Spike	Field Reagent Spike	Lab Reagent Spike
Field Sources:				
Field environment:				
Water matrix interference	T	T		
Shipping to lab:				
Analyte degradation	T		T	
Laboratory Sources:				
Lab environment/Analysis	T	x	x	T

Field Matrix Spike Example

Compare 1 Field Matrix Spike to 40 NWQL Lab Reagent Spikes (1995)

Compound	NWQL Mean Recovery (percent)	NWQL Standard Deviation (percent)	Lower 95% Conf Limit (percent)	Upper 95% Conf Limit (percent)	Field Matrix Spike Recovery (percent)
Atrazine	102.2	2.7	96.9	107.6	109.8
Diazinon	82.2	1.1	80.0	84.5	83.0
Malathion	93.2	16.6	60.1	126.3	56.2

- Perhaps a matrix effect (or degradation for Malathion)
- Talk with chemists, do another field matrix spike to confirm.

Poor Recovery Examples

- A field matrix spike with 25% recovery
- Do I have a problem? Maybe. Examine lab reagent spike recovery
- To locate problems, need sets of basic and topical QC samples
- 4 simple examples of poor recovery

Poor Recovery Example - 1

Spike Type	Recovery (percent)
Field Matrix Spike	25
Lab Reagent Spike	100
Field Reagent Spike	100
Lab Matrix Spike	25

- What is the cause of 25 % recovery in Field Matrix Spike?

Matrix effect

Poor Recovery Example - 2

Spike Type	Recovery (percent)
Field Matrix Spike	25
Lab Reagent Spike	100
Field Reagent Spike	25
Lab Matrix Spike	100

- What is the cause of 25 % recovery in Field Matrix Spike?

Degradation

Poor Recovery Example - 3

Spike Type	Recovery (percent)
Field Matrix Spike	25
Lab Reagent Spike	100
Field Reagent Spike	50
Lab Matrix Spike	50

- What is the cause of 25 % recovery in Field Matrix Spike?

Matrix effect and degradation

Poor Recovery Example - 4

Spike Type	Recovery (percent)
Field Matrix Spike	25
Lab Reagent Spike	25
Field Reagent Spike	25
Lab Matrix Spike	25

- What is the cause of 25 % recovery in Field Matrix Spike?
  - Typical method performance

Comments on Spikes

- For Matrix spikes you also need an unspiked sample to correct for background concentrations
- Causes of poor recovery are never as clear as in the examples
- Do more Field Matrix Spikes to confirm poor recovery in a particular matrix

Comments on Spikes - 2

- If concentrations in your environmental samples are much higher or lower than the "normal" concentrations spiked, consider spiking at concentrations important for your study
- Much more uncertainty in estimates of recovery when spiked concentrations are less than or equal to background concentrations. Better to spike at 2-5 times background.

Questions on Spikes?

Reference Samples

- Samples of known concentration that are used to measure performance (bias) of the analytical method.
- Variability can be estimated if the same reference sample is measured multiple times by the same analytical method
- Reference samples are often used to assess comparability of methods or labs

Reference Samples

Type	Targeted Source of Bias	Use
Reference	Method Performance	Topical

- Not usually submitted by field crews unless (1) the laboratory doesn't have a good QC program or (2) you have unusual concentrations that are not QC'd by the laboratory.

Document What Was Measured

- Because HOW a QC sample was collected makes big differences in the sources of error measured...Keep detailed field notes on:
  - What you intended to measure
  - How you measured it
- You will forget!

Summary on QC Sample Types

- Good science requires assessment of measurement errors (bias and variability) for data analysis and interpretation
- BASIC QC Samples are used to estimate the quality of the environmental data because they measure all of the sources of error that affect environmental samples
- Basic QC samples are the most important to collect
- TOPICAL QC samples are used (if needed) in sets to locate the cause of data-quality problems

Questions?

Questions?

- Had enough yet?