The Abdus Salam
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The International Union of Geodesy and Geophysics

United Nations
Educational, Scientific and
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2339-1

Workshop on Atmospheric Deposition: Processesand Environmental Impacts

21 - 25 May 2012

Quality Assurance and Quality Control for Wet Deposition Monitoring

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Quality Assurance and Quality Control for Wet Deposition Monitoring

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Acronyms for Lecture – 1/2

- **ACM –** AeroChem Metrics 301 precipitation collector
- **AIRMoN** – Atmospheric Integrated Research Monitoring Network
- **CAL –** Central Analytical Laboratory at University of Illinois, USA
- **DQOs** – Data Quality Objectives
- ***f*ps** – *f*-pseudosigma = (75^{th} percentile – 25^{th} percentile)/1.349,
  = non-parametric analogue of standard deviation
- **HAL –** Mercury (Hydragyrum) Analytical Laboratory at
  Frontier Global Sciences, Bothel, Washington, USA
- **LCL –** Lower Confidence Limit
- **MDL** – Method Detection Limit
- **MDN –** Mercury Deposition Network: total Hg
- **MPV –** Most Probable Value (Median, 50^{th} percentile)
- **MRL** – Method Reporting Limit
- **NADP –** National Atmospheric Deposition Program
- **N-CON –** N-CON Systems Precipitation Collector
- **NMCL –** Network Maximum Contamination Level

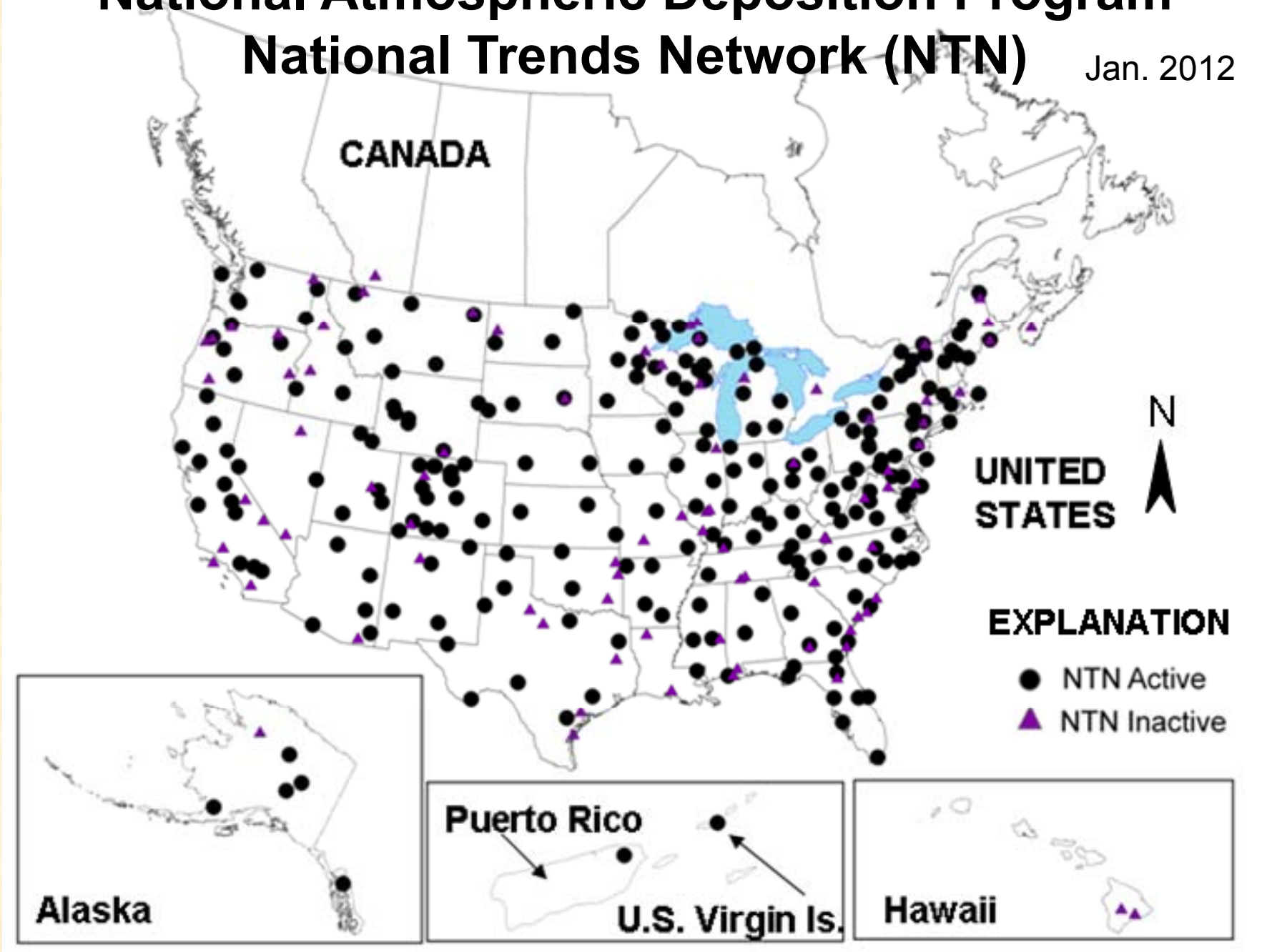
Acronyms for Lecture – 2/2

- **NTN** – National Trends Network: pH, N_{rxn}, SO_4^{2-}
- **PRISM –** Parameter-elevation Regression on Independent Slopes Model, Oregon Climate Center, Oregon State Univ.
- **QA** – Quality Assurance
- **QC** – Quality Control
- **QAP** – Quality Assurance Plan
- **QMP** – Quality Management Plan
- **RSD** – Relative Standard Deviation
- **SOP** – Standard Operating Procedure
- **UCL** – Upper Confidence Limit
- **USEPA –** United States Environmental Protection Agency
- **USGS –** United States Geological Survey (Dept. Interior)

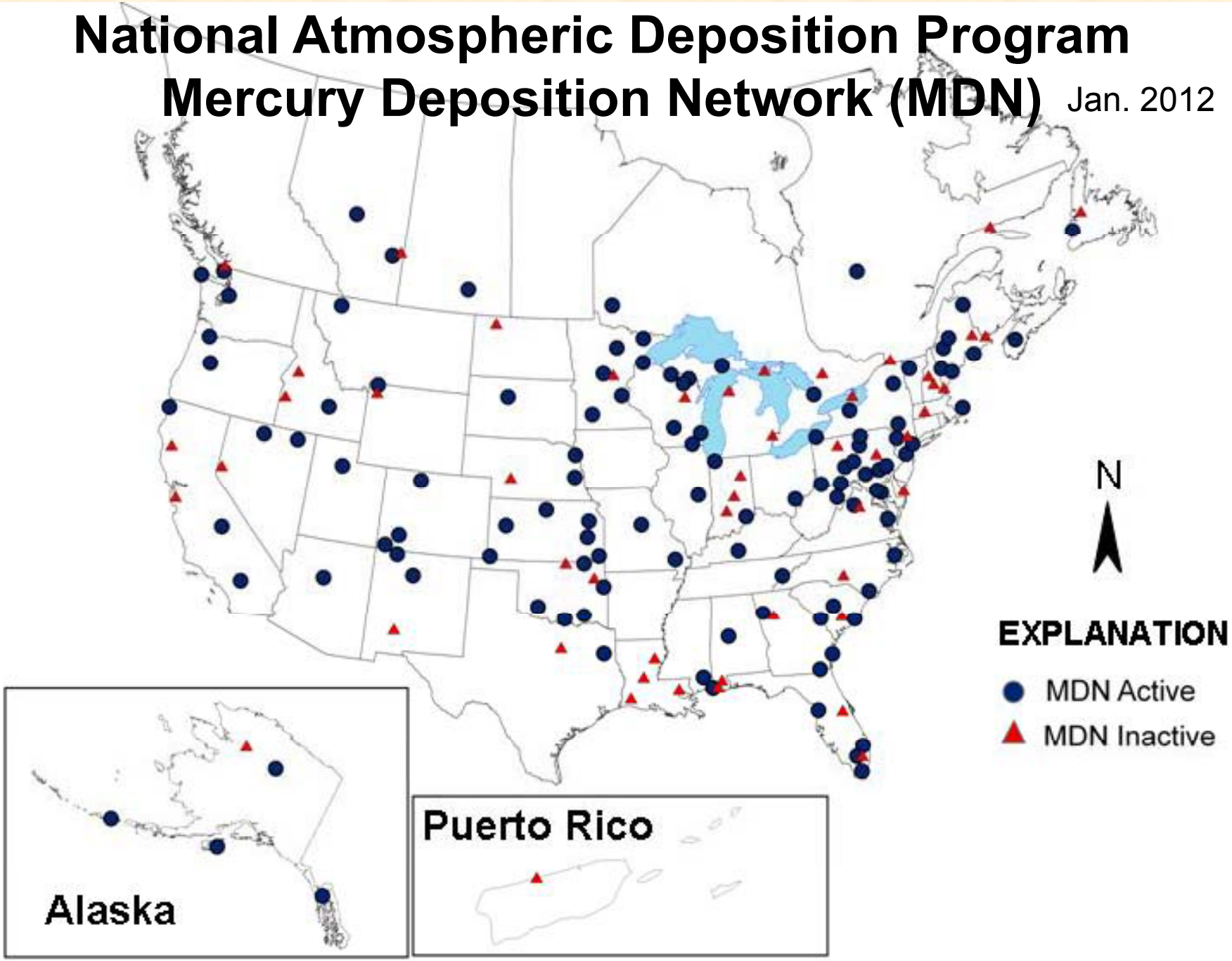
National Atmospheric Deposition Program QA/QC Overview

National Atmospheric Deposition Program
National Trends Network (NTN)

Jan. 2012



National Atmospheric Deposition Program
Mercury Deposition Network (MDN) Jan. 2012



NADP QA/QC

National Atmospheric Deposition Program

- **NADP Program Office – QA Manager**
  - Overall audit and documentation of NADP data-collection, management, and reporting systems
- **Laboratory internal QC samples & studies**
  - Central Analytical Laboratory = NTN, AIRMoN, AMoN
  - Mercury Analytical Laboratory = MDN
- **USGS external QC programs** – 3rd party evaluation
- **USEPA external Site Audit Program** – 3rd party

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Quality Assurance (QA)

- Procedures, documentation, and audits used to control components of a project to achieve objectives.

Quality Control (QC)

- Data collected and analyzed to estimate bias and variability of measurements.

Analyze QC data to achieve QA.

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Quality Assurance (QA)

- Implement Controls for Measurements:

  locations – regional representation
  collection time – event, weekly, bi-weekly
  standardized equipment
  standardized techniques
  promote sample integrity – preservation
  promote sample validity, limit contamination?

Quality Control (QC)

- Collect data to challenge / evaluate data-collection systems:

  Does location affect data collected?
  Does equipment perform properly?
  Do techniques preserve sample integrity?
  Do laboratories produce accurate data?
  Are network changes influencing bias?

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NADP Program Documents

QA ONLY EXISTS
WHEN DOCUMENTED!

QA Program Plan
Site Operations Manuals = Field Protocols
Laboratory QA Program Plans
Laboratory Standard Operating Procedures
Documented Laboratory Methods
Data Validation Protocols
Laboratory QA Reports - Annual
External (USGS) QA Program Reports - Biannual

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Sample Validation

- Check visibly contaminated samples (e.g. plants, insects, soot, other) for high concentrations.
- Collector was NOT open during periods with no precipitation ("Dry Exposure")
- Collector operated properly

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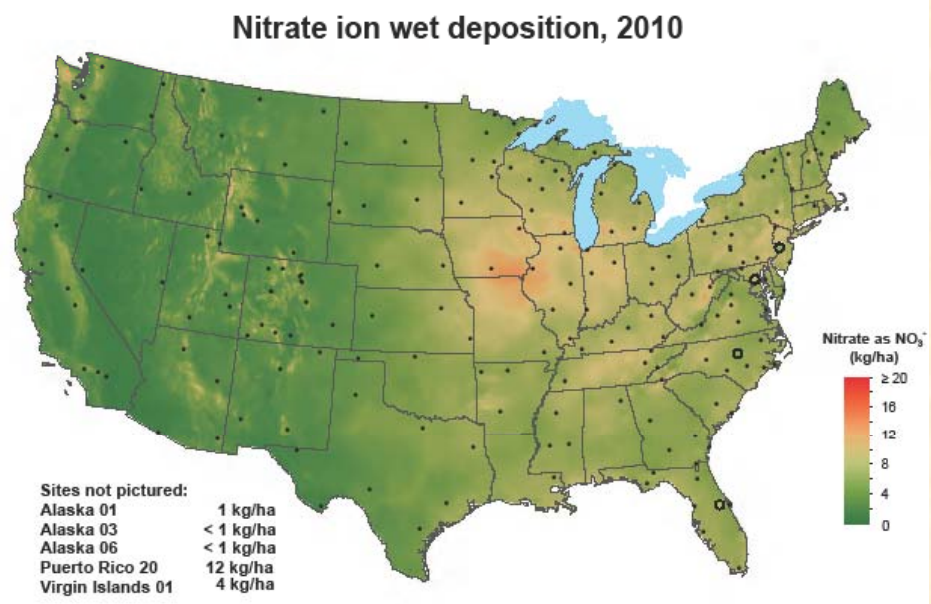
NADP Data Products

- Data from a site may only be used for NADP map products if :

1) Valid 75% of the year
2) Valid 90% of the annual precipitation depth
3) Precipitation data for 75 % of the time period



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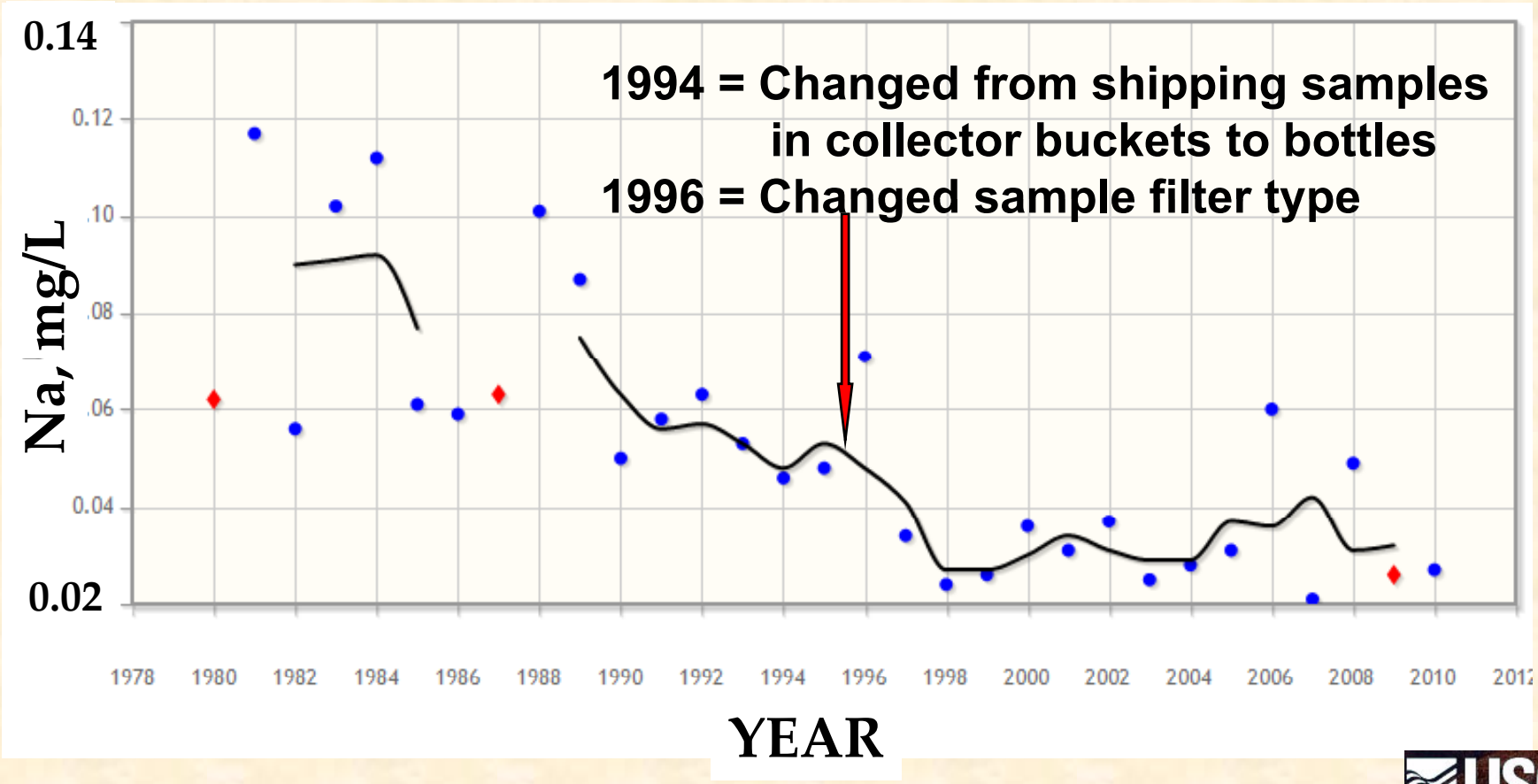
QA/QC Objectives

Overall QA/QC Objective

- Ensure that temporal and spatial trends represent environmental signals and are quantified within "*acceptable*" error limits.



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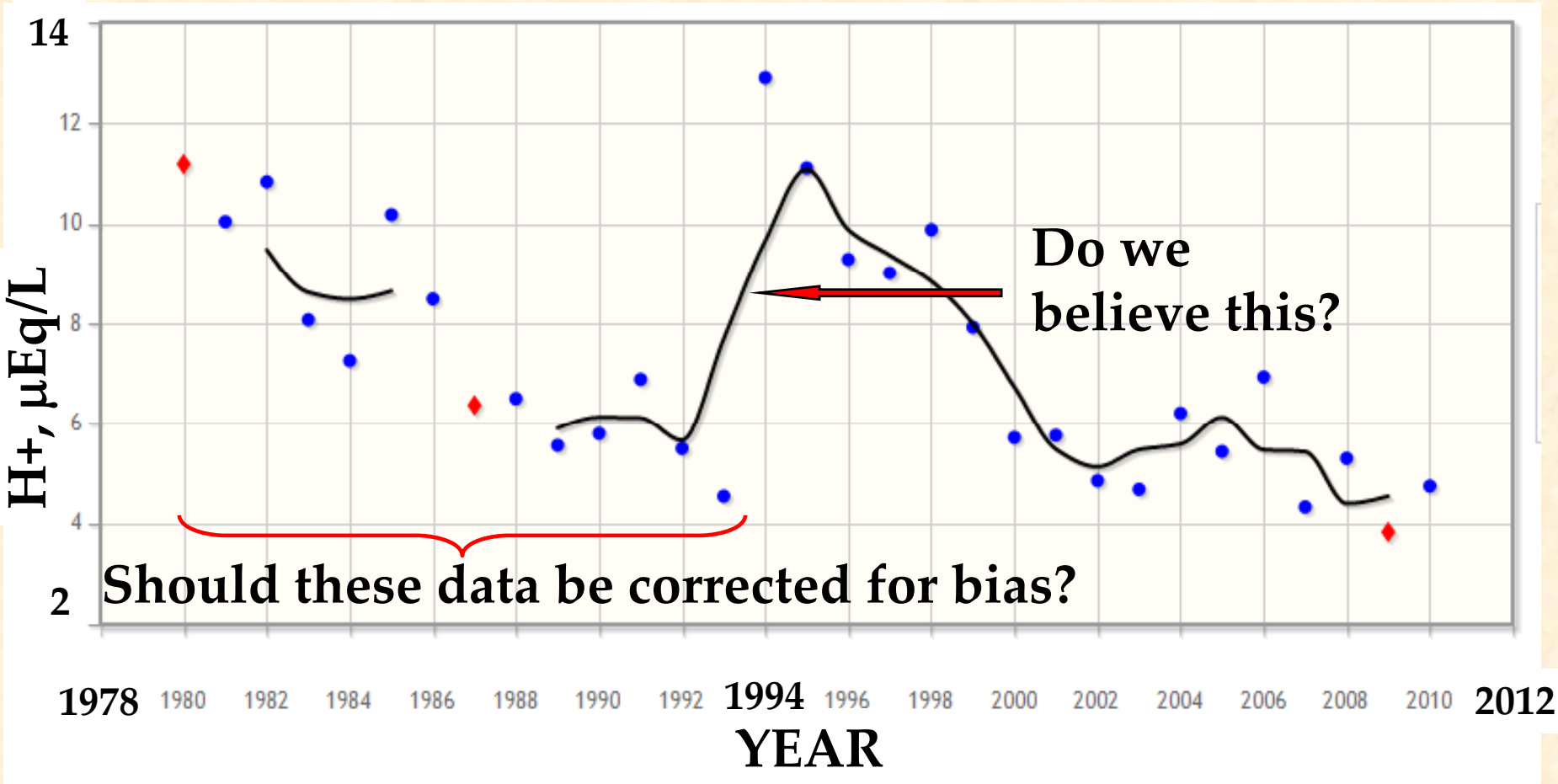
QA/QC Objective

1994 = Changed from shipping samples in collector buckets to bottles
1996 = Changed sample filter type



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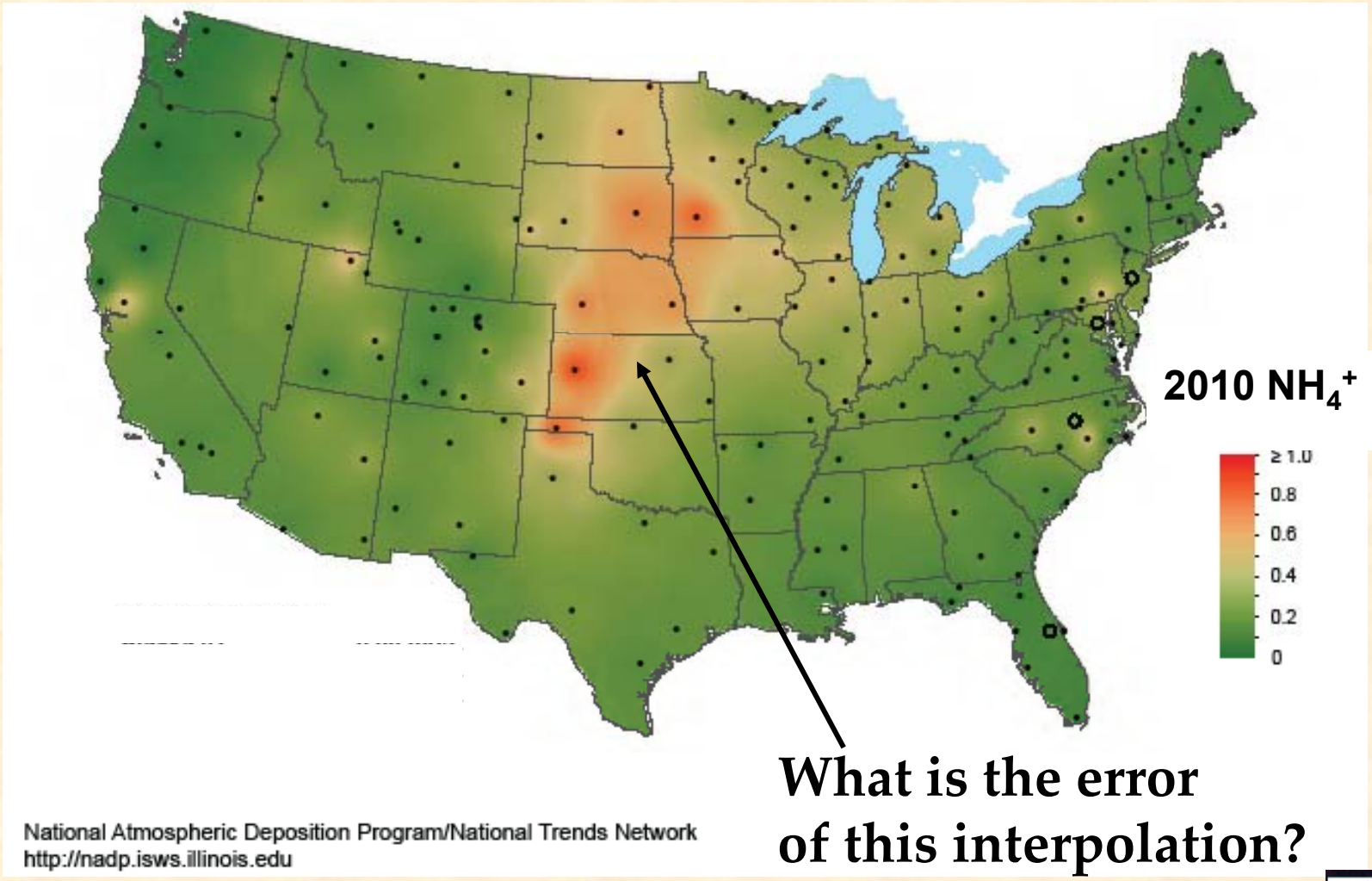
Spatial Data Products QA/QC

Valid samples ☑ **Complete data** ☑

How representative is this map?



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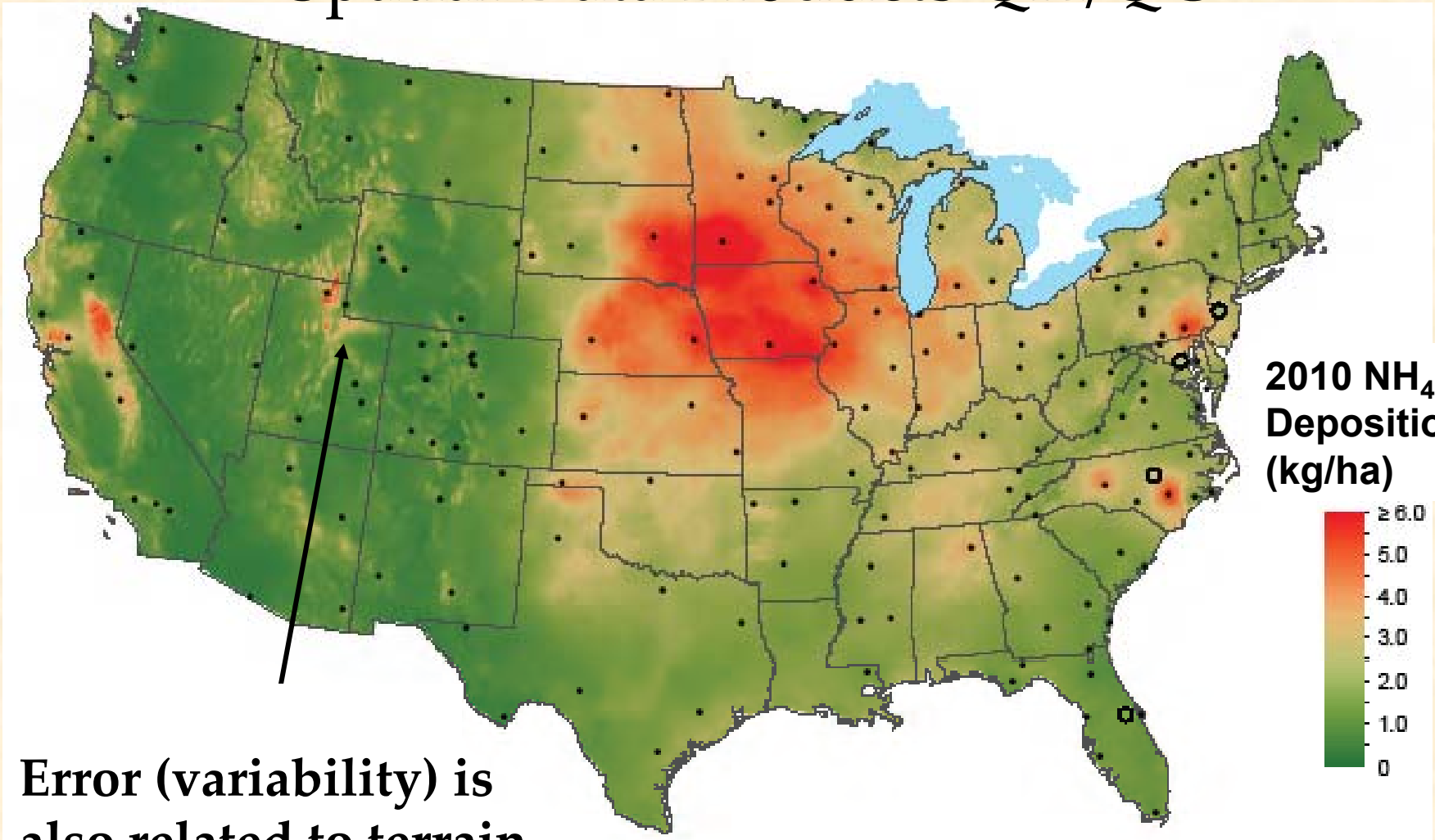
Spatial Data Products QA/QC



Error (variability) is also related to terrain.

Example: Ammonium deposition in Rocky Mountains

Deposition = PRISM (ppt) X NADP Concentration

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Quality Control (QC) Requires Data

Measure 2 components of error in environmental data:

- Bias: Positive or negative systematic error in measurements. (Relative Accuracy)
- Variability: Random inherent error as a result of repeated application of the measurement process under controlled conditions. (Absolute Precision)

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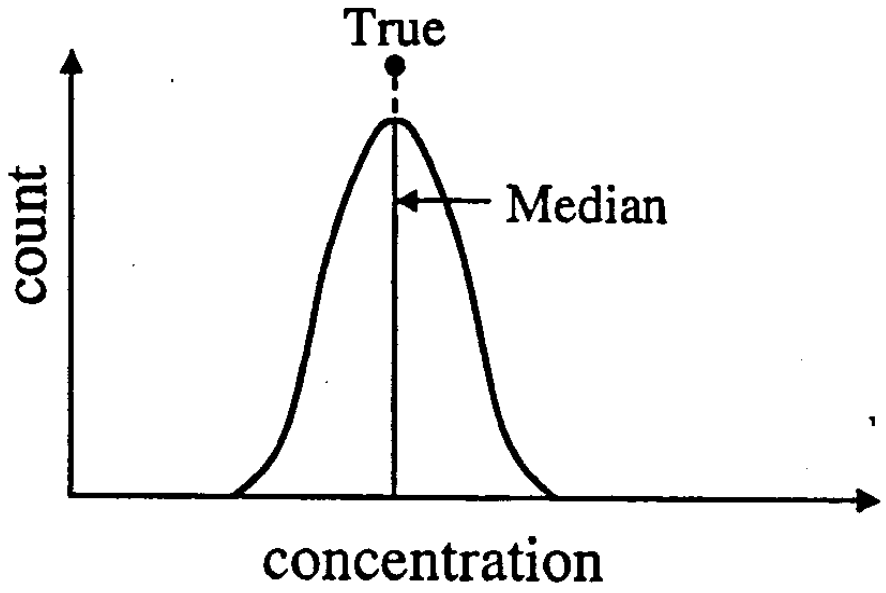
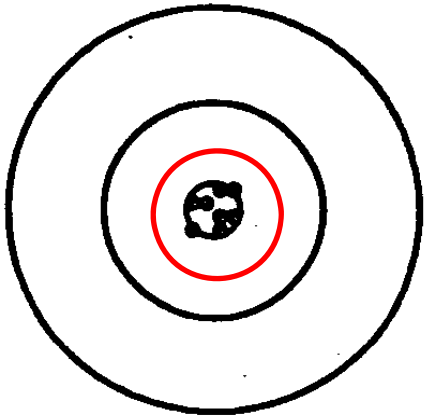
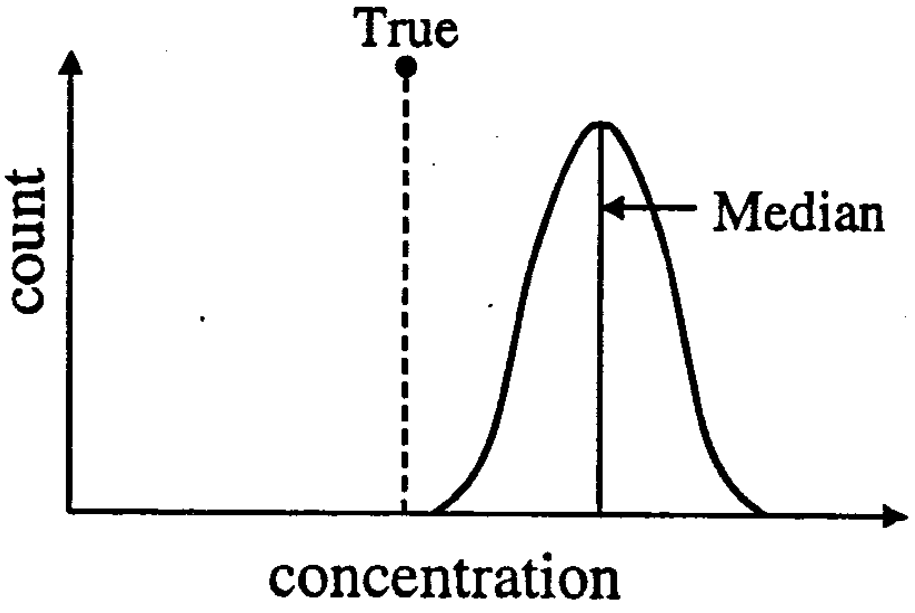
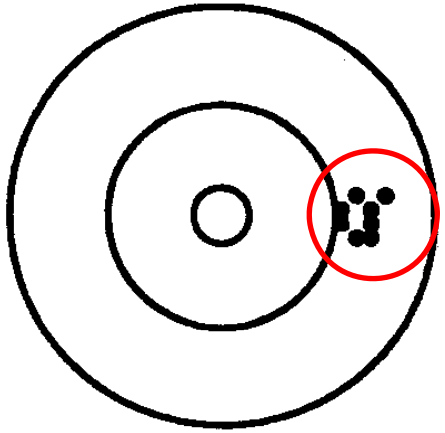
Low Bias & Low Variability



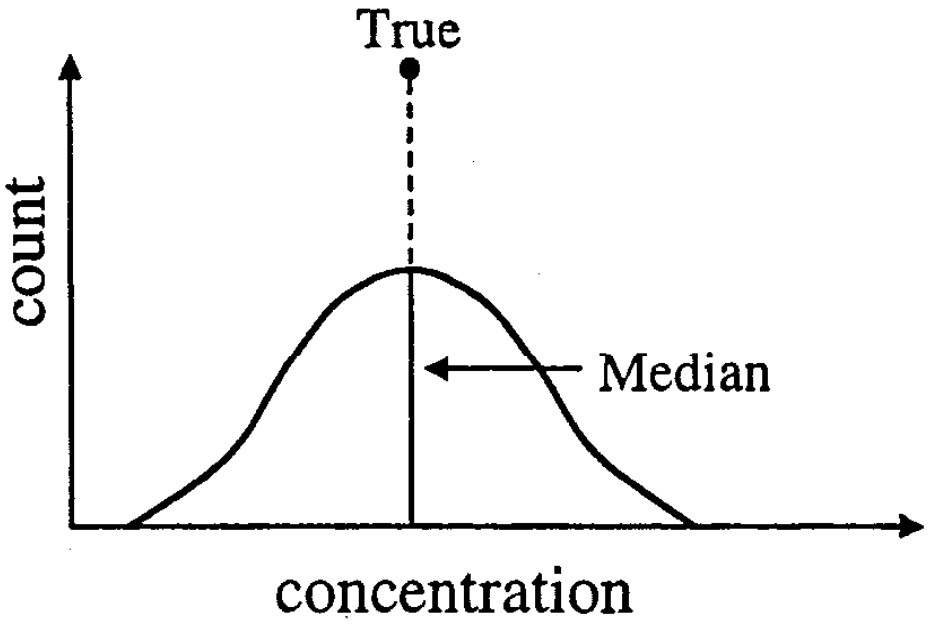


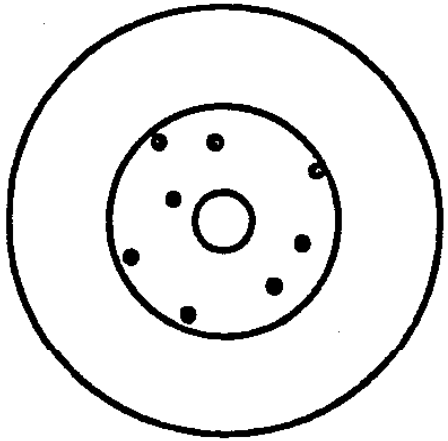
High Bias & Low Variability



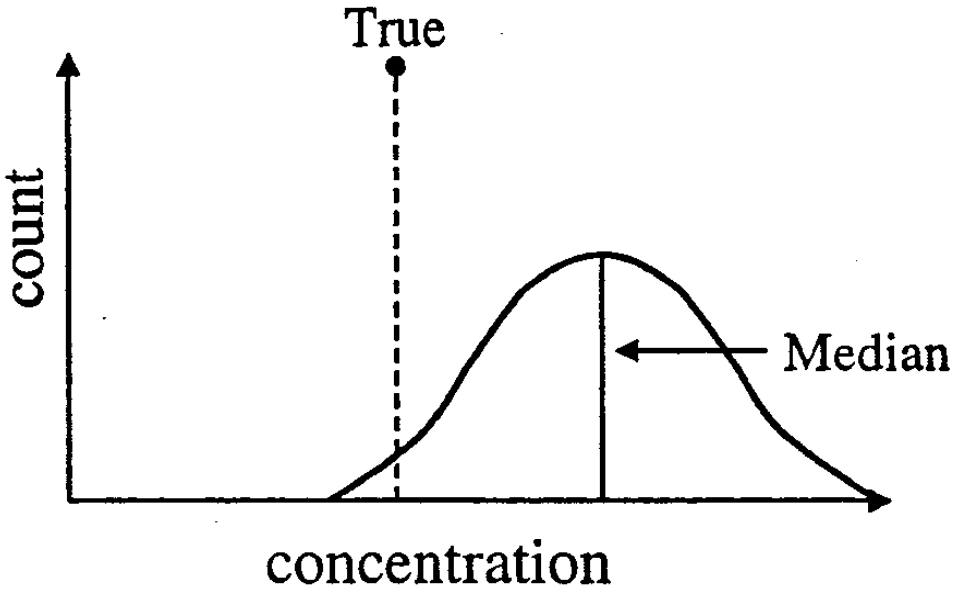


Low Bias & High Variability





High Bias & High Variability



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Common Sources of Wet-Deposition Bias ... & *Variability*

Sample Contamination – **bird droppings**,

debris, dust, insects
operators/people,
laboratory

Sample Evaporation – bi-weekly > weekly > event

Sample Stability – N, P, H^+ (pH), Hg

Collector Catch Efficiency –partial events typical

Raingage bias – false positives, debris, insects,
chart vs electronic

QC Sample Types / Purpose

Blanks — **2 Types: Laboratory & Field / Bias**

Spikes — **Laboratory & Field / Bias**

Reference Materials — **Laboratory & Field / Bias**

Laboratory Replicates — **Laboratory Variability**

Co-Located Sampler Replicates — **Overall Variability**

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Quantifying Bias and Variability in NADP Measurements

Internal NADP QC Programs

Interlaboratory-Comparisons

- Laboratory variability and bias

Field Supply Blanks – Before Field Exposure

- Collector bucket blanks
- Sample bottle blanks
- Bag blanks
- Filter blanks

Special Studies

- Bias from factors affecting sample integrity
- Bias from instrumentation performance

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External USGS QA/QC Programs

Field Supply Audits – Post Field Exposure

Bias from sample contamination or instability

Co-Located Collector Studies

2 Identical Collectors = Overall Variability

2 Different Collectors = Overall Bias from Instrument Changes

Interlaboratory-Comparisons

Laboratory variability and bias

Special Studies

Bias affecting sample integrity, representation

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External USGS QA/QC Programs

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2 USGS INTERLABORATORY COMPARISON PROGRAMS

Ca, Mg, Na, K, NH4,
Cl, Br, NO3, SO4,
pH, Specific Conductance

4 samples / month

7 labs in 4 countries:
USA, Canada,
Norway, Japan

Total Hg by CVAF

2 samples / month

11 labs:
USA, Canada, Sweden,
Belgium, Taiwan, Germany,
Slovenia, China

Pending: IT, FR, SA

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External USGS QA/QC Studies

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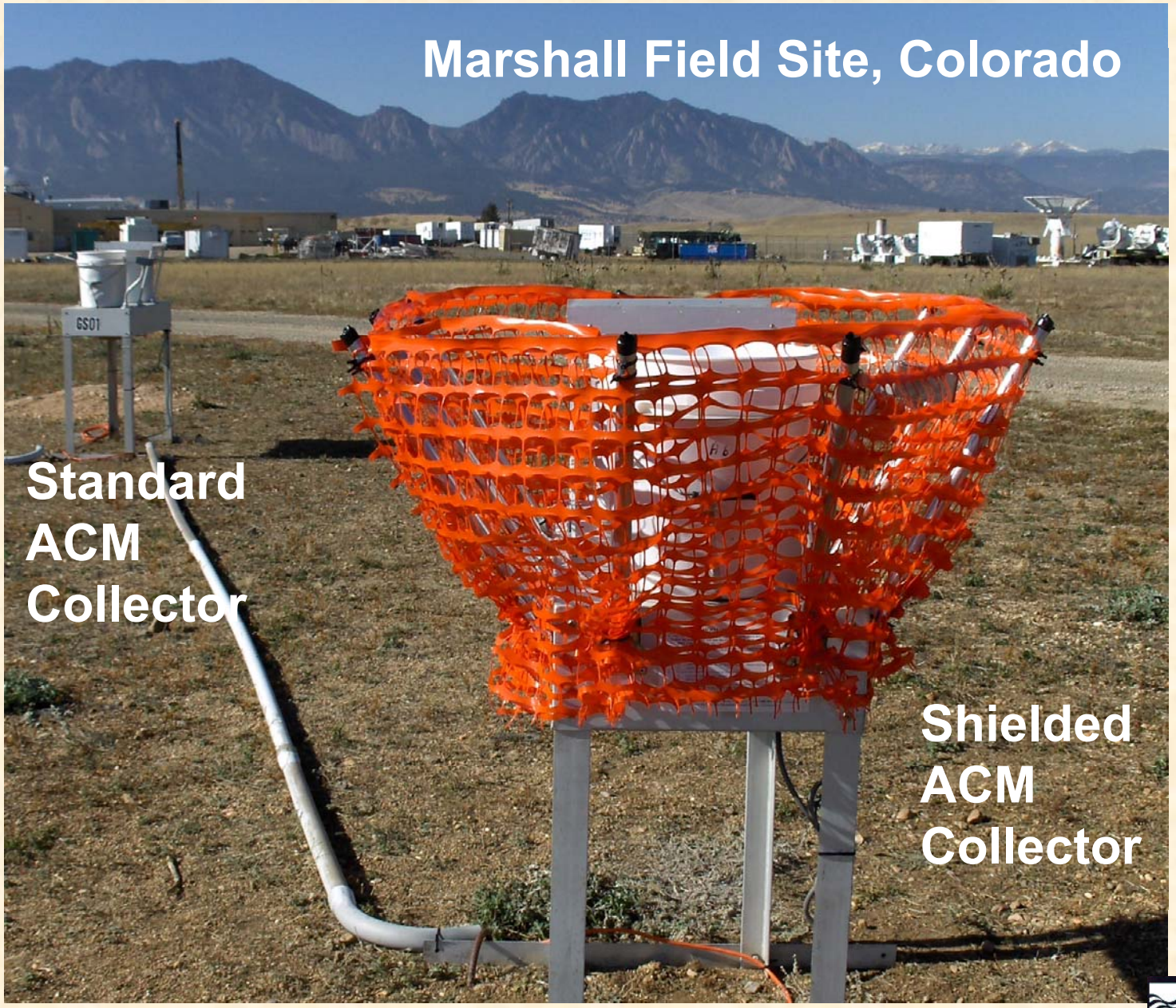
Marshall Field Site, Colorado
Standard
ACM
Collector
Shielded
ACM
Collector
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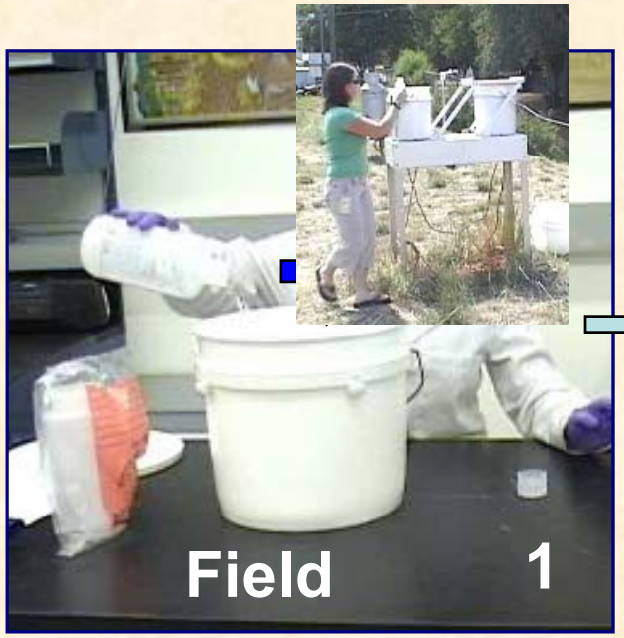
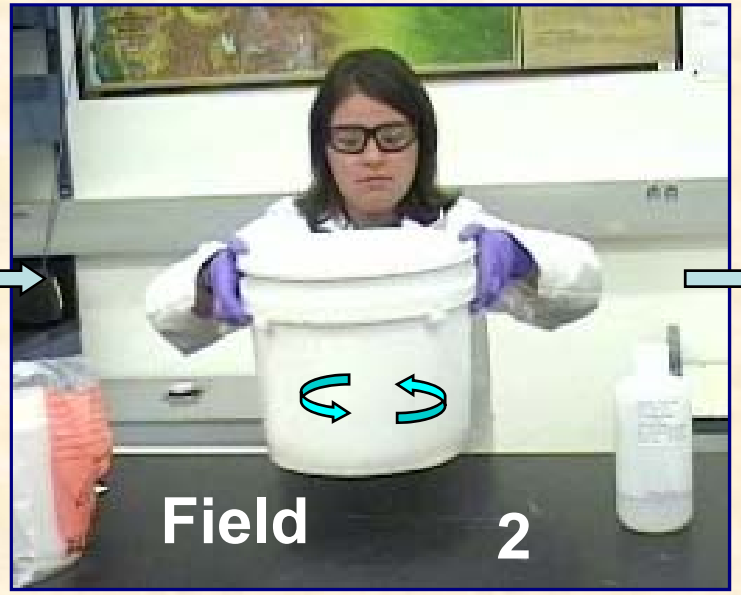
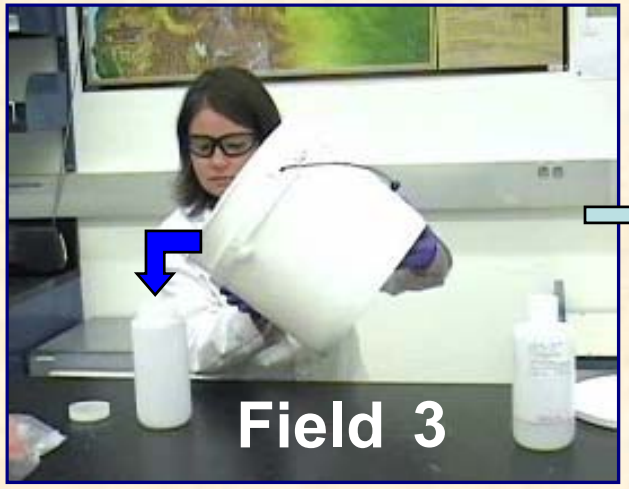
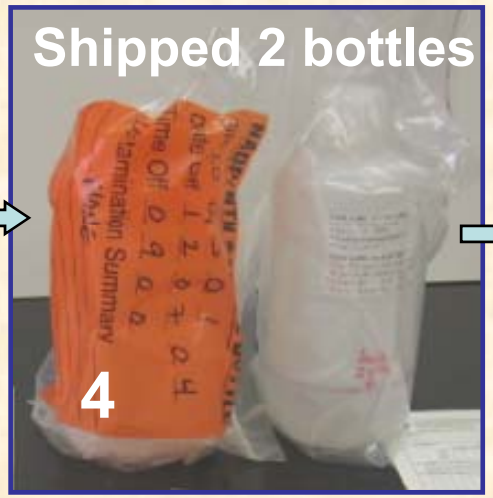
Bias

NTN Field Audit









NTN Field Audit & MDN System Blank

What is the maximum **contamination** that we can expect in NTN and MDN samples with statistical confidence?

Network Maximum Contamination Level
= 90% UCL of [Contamination]
with 90% confidence

What is the maximum **analyte loss** that we can expect in NTN and MDN samples with statistical confidence?

= 90% UCL of [Analyte Loss] with 90% confidence

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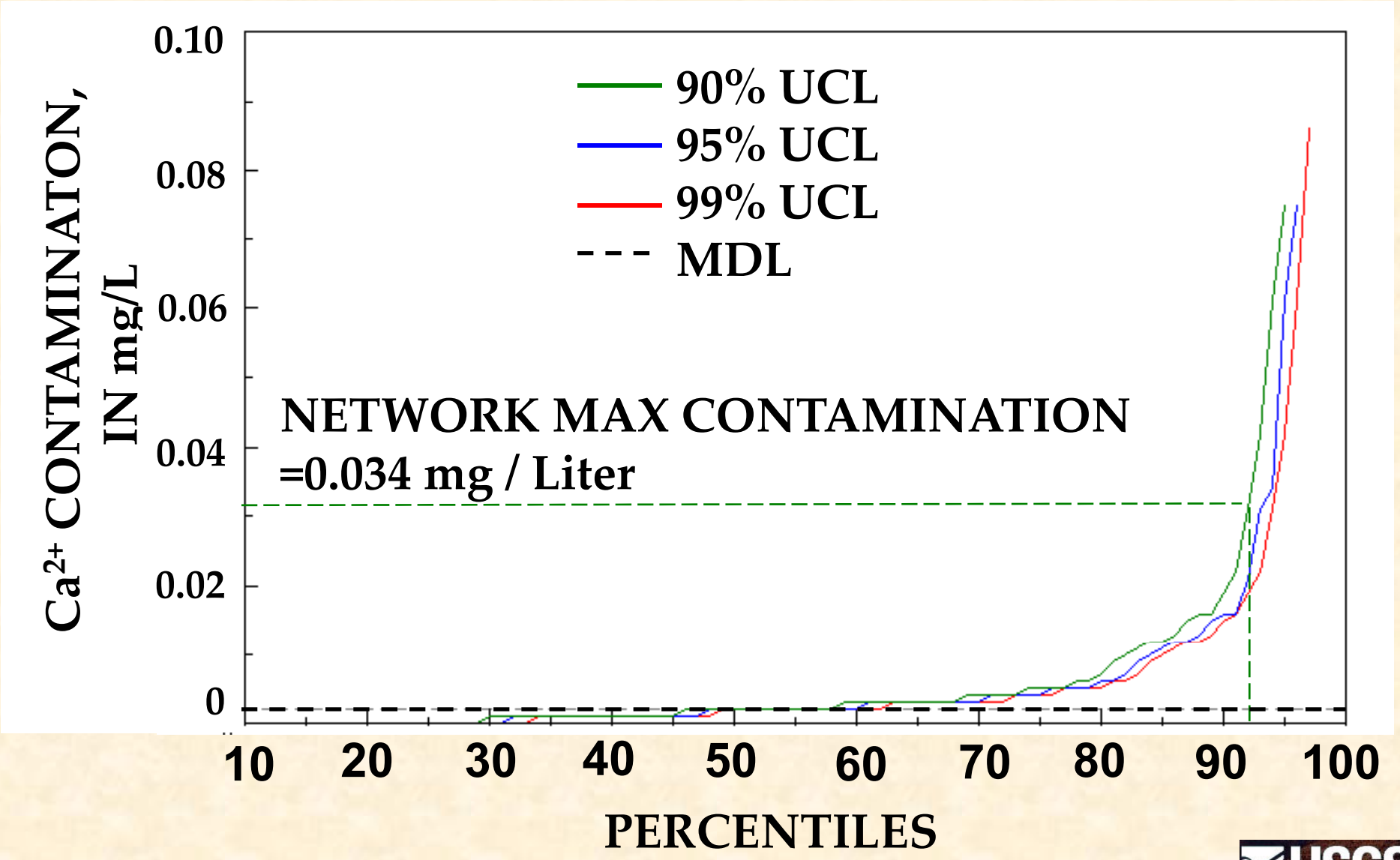
Bucket – minus - Bottle Ca^{2+}
CONTAMINATION IN NTN SAMPLES, 2009-11



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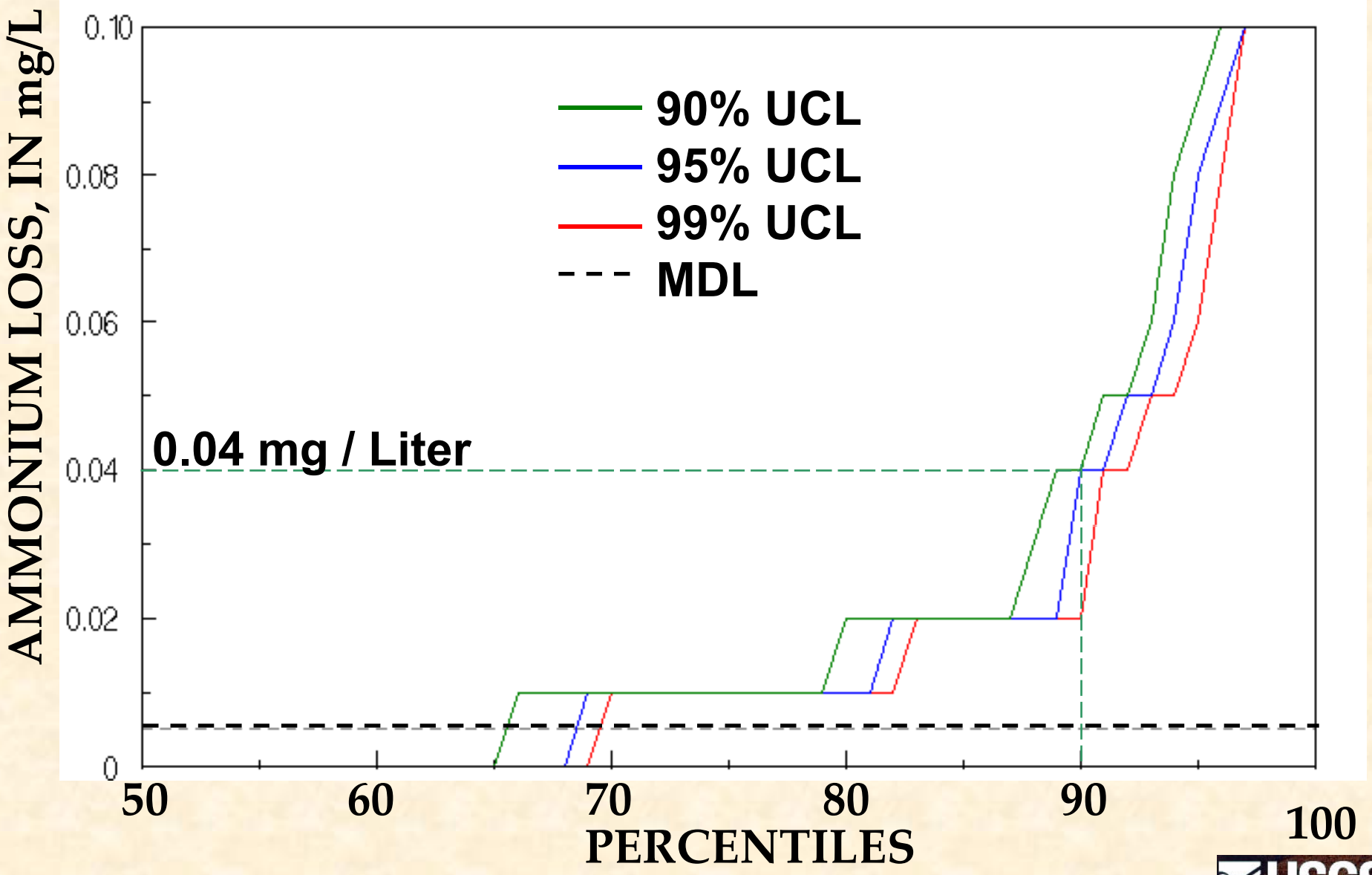
Bottle – minus – Bucket
NH_4^+ LOSS IN NTN SAMPLES, 2009-11



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2011 Field Audit
2009-11 Network Maximum Contamination Levels & Ptiles

Analyte	NMCL	NTN %tile
Ca^{2+}(mg/L)	0.034	16
Mg^{2+} (mg/L)	0.006	15
Na^{+} (mg/L)	0.015	21
K^{+} (mg/L)	0.007	18
NH_4^{+} (mg/L)	0.020	40
Cl^{-} (mg/L)	0.025	11
NO_3^{-} (mg/L)	0.044	1
SO_4^{2-} (mg/L)	0.030	1
H^{+} (μEq/L)	1.2	17

N = 330 sample pairs

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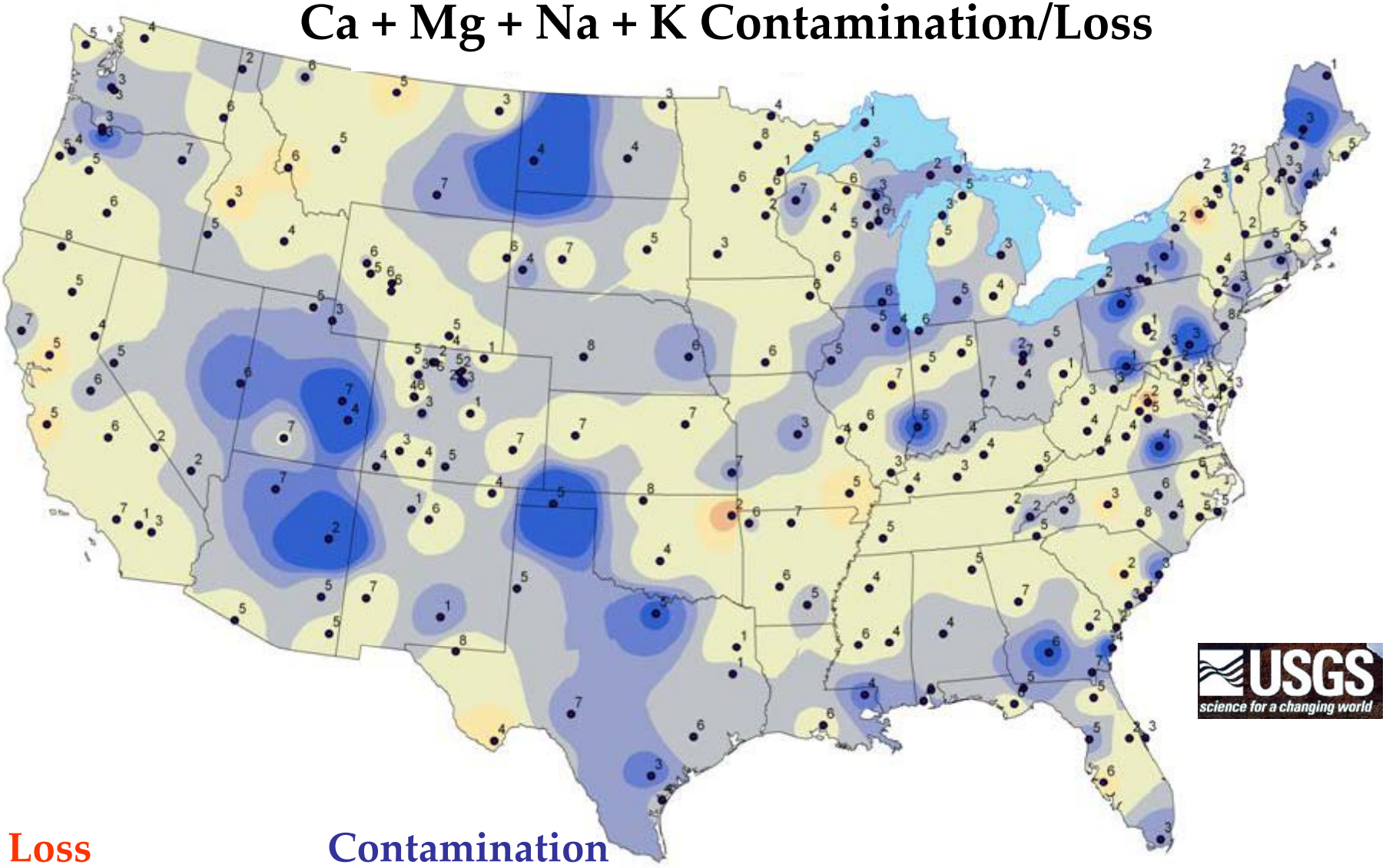
Ca + Mg + Na + K Contamination/Loss



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Loss

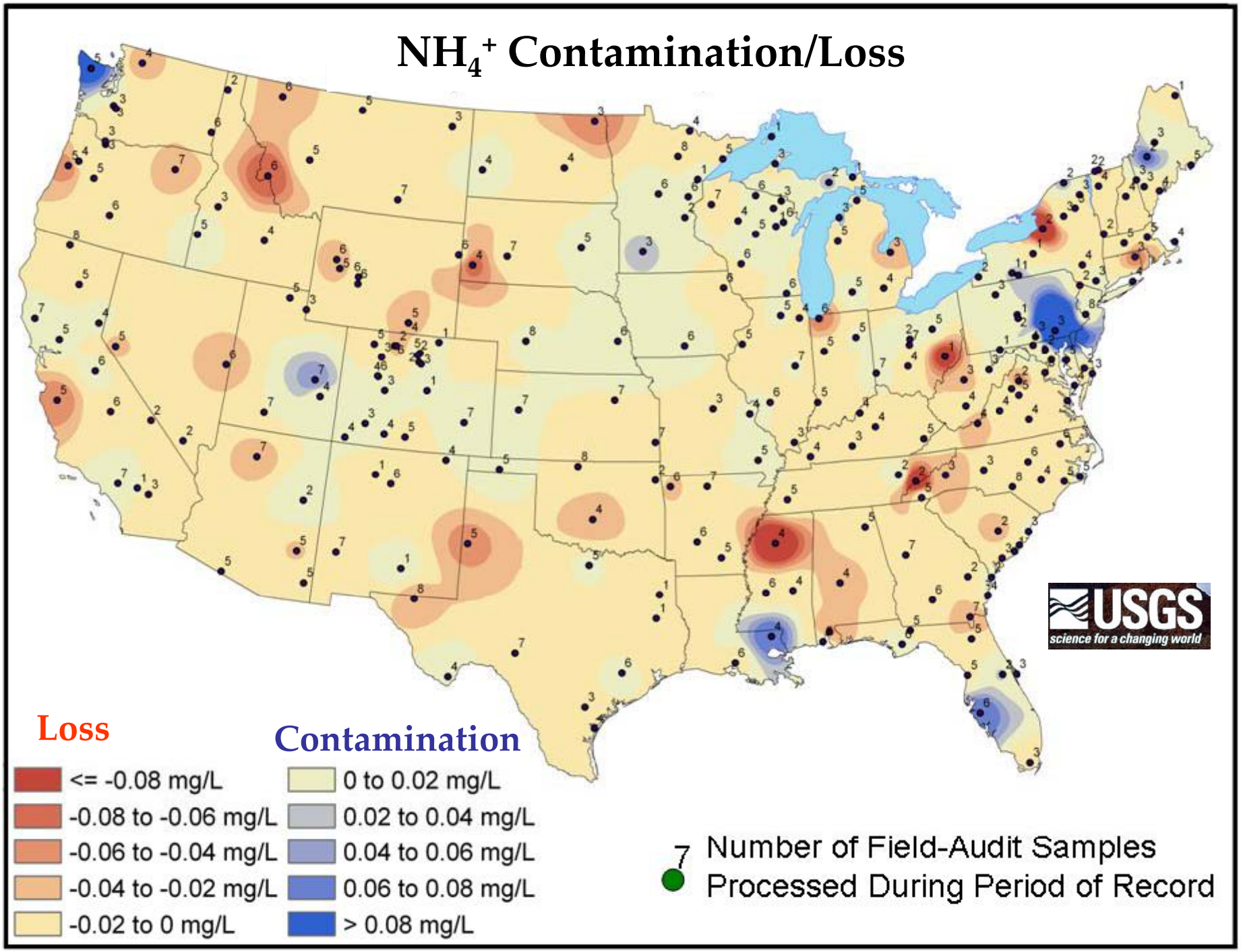
- -0.003 to -0.002 meq/L
- -0.002 to -0.001 meq/L
- -0.001 to 0 meq/L
- 0 to 0.001 meq/L

Contamination

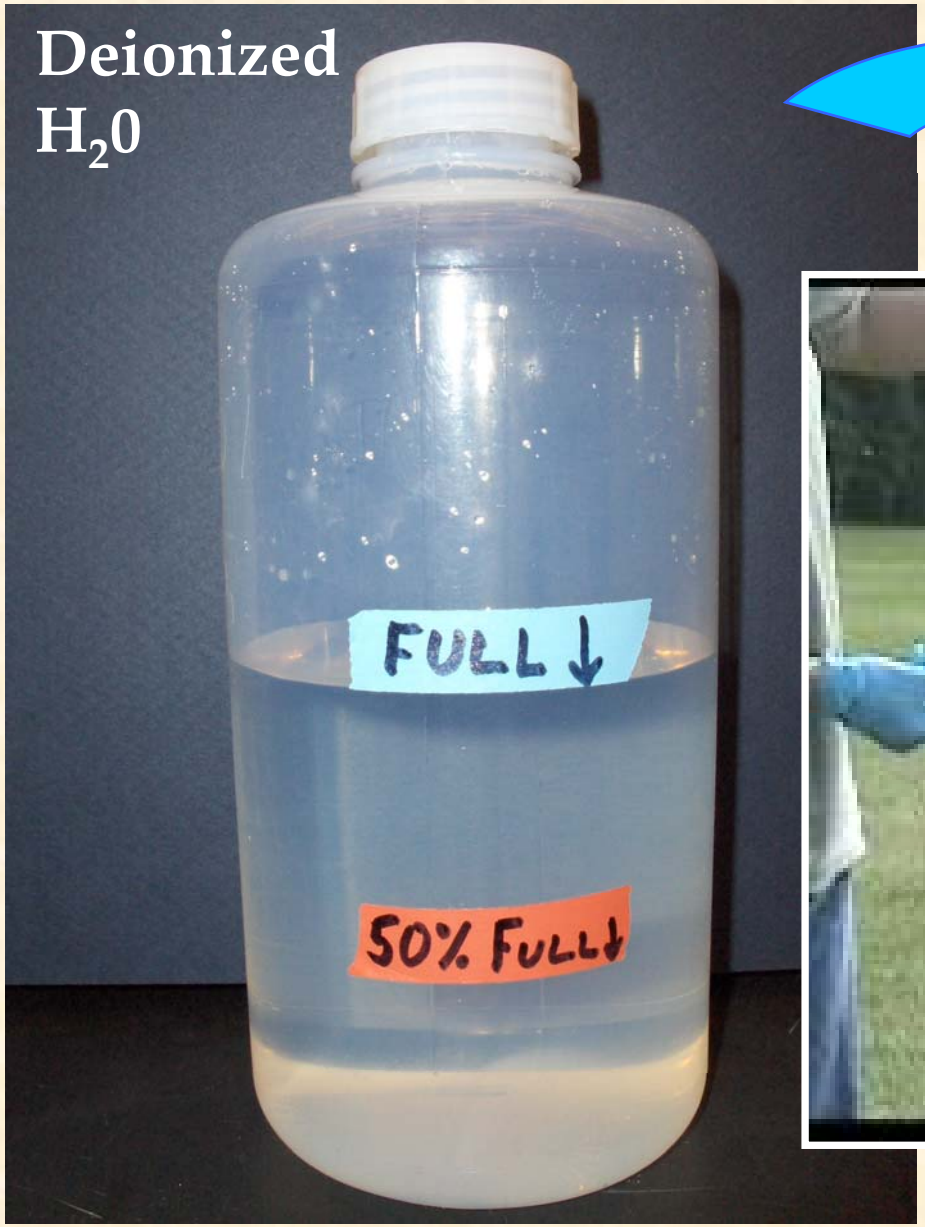
- 0.001 to 0.002 meq/L
- 0.002 to 0.003 meq/L
- 0.003 to 0.004 meq/L
- > 0.004 meq/L

7 Number of Field-Audit Samples Processed During Period of Record

NH_4^+ Contamination/Loss



MDN SYSTEM BLANK



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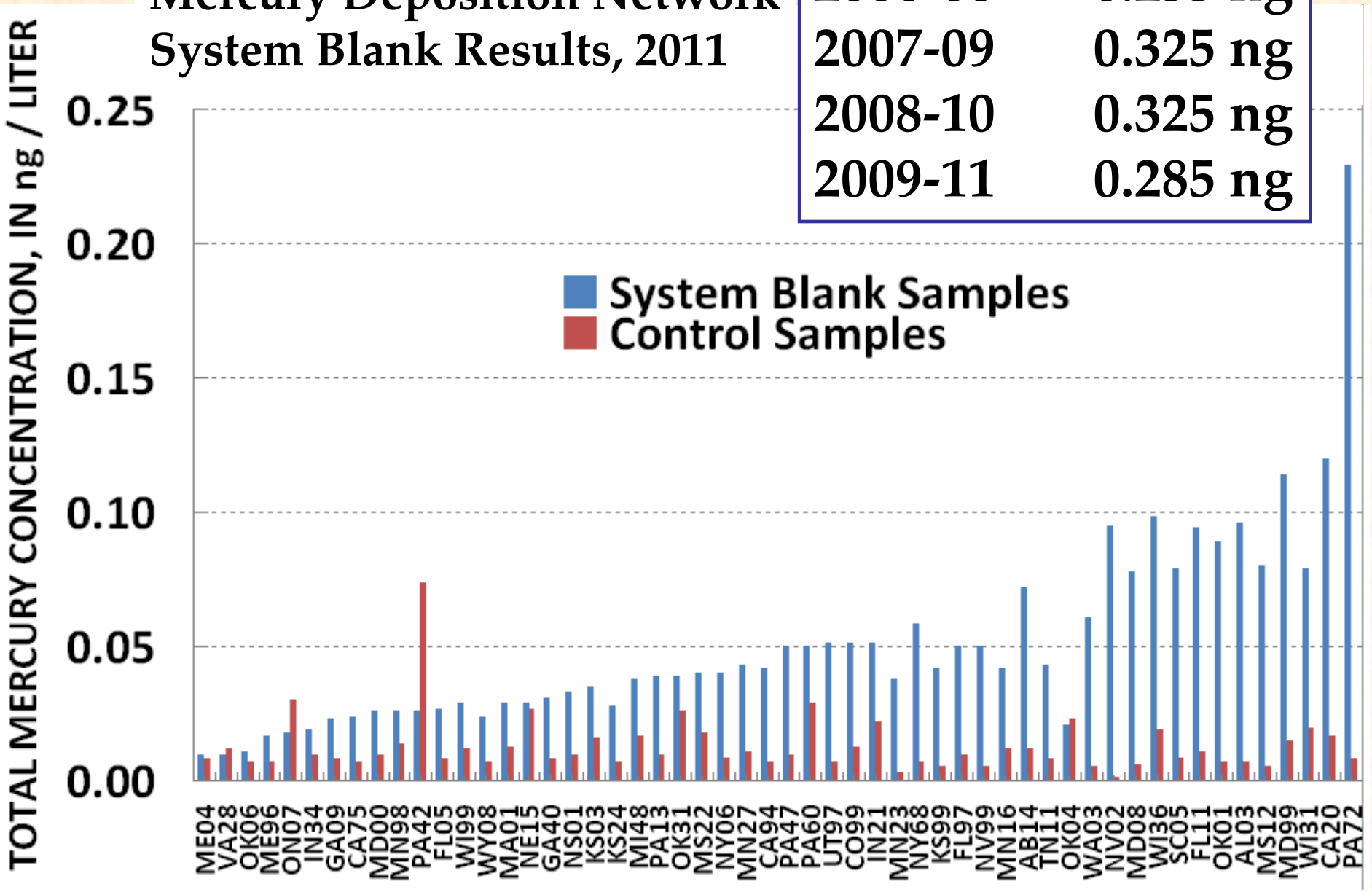
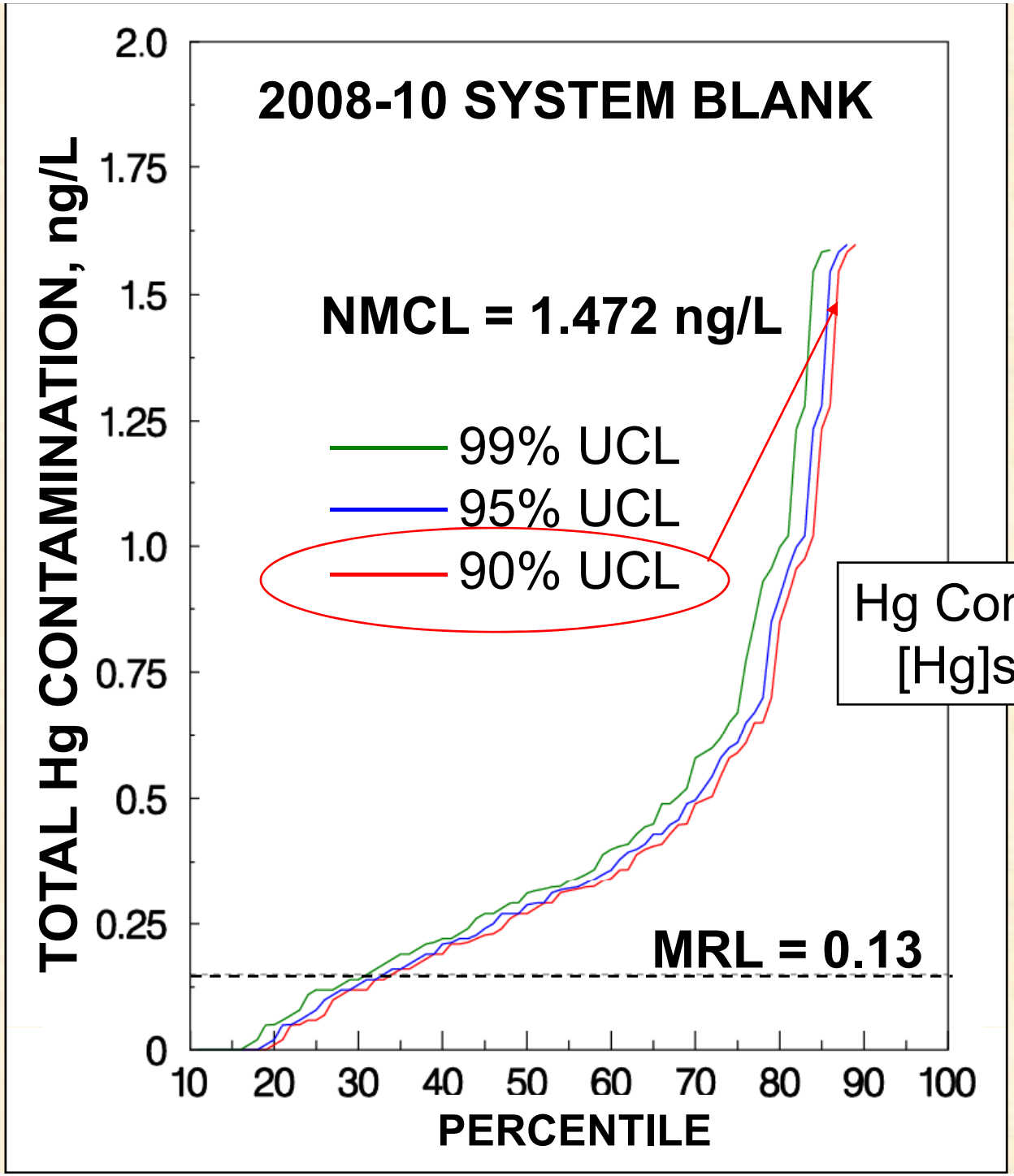
Mercury Deposition Network System Blank Results, 2011

MDN NMCL's	
2006-08	0.233 ng
2007-09	0.325 ng
2008-10	0.325 ng
2009-11	0.285 ng





Hg Contamination =
[Hg]system – [Hg]bottle

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USGS PROGRAM Hg LABORATORIES

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Most Probable Value (MPV)

MPV = median, 50th percentile value

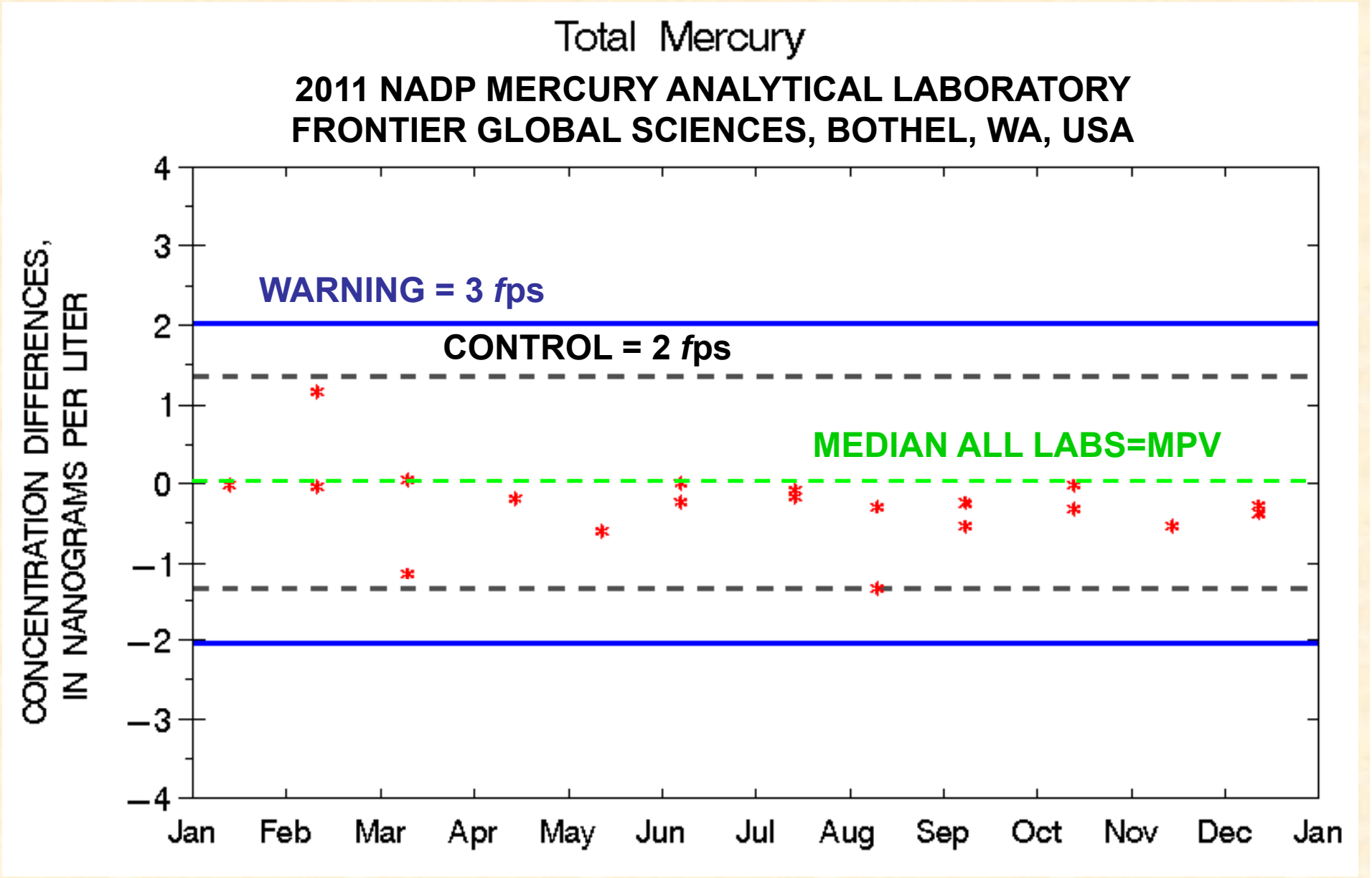
f-pseudosigma

*f*ps = 75th ptile – 25th ptile / 1.349

A non-parametric analogue of standard deviation

±1 *f*ps = 67% of values
±2 *f*ps = 95% of values
±3 *f*ps = 99% of values

Hoaglin, D.C., Mosteller, F., and Tukey, J.W., 1983, Understanding robust and exploratory data analysis: New York, John Wiley and Sons, p. 38-41.



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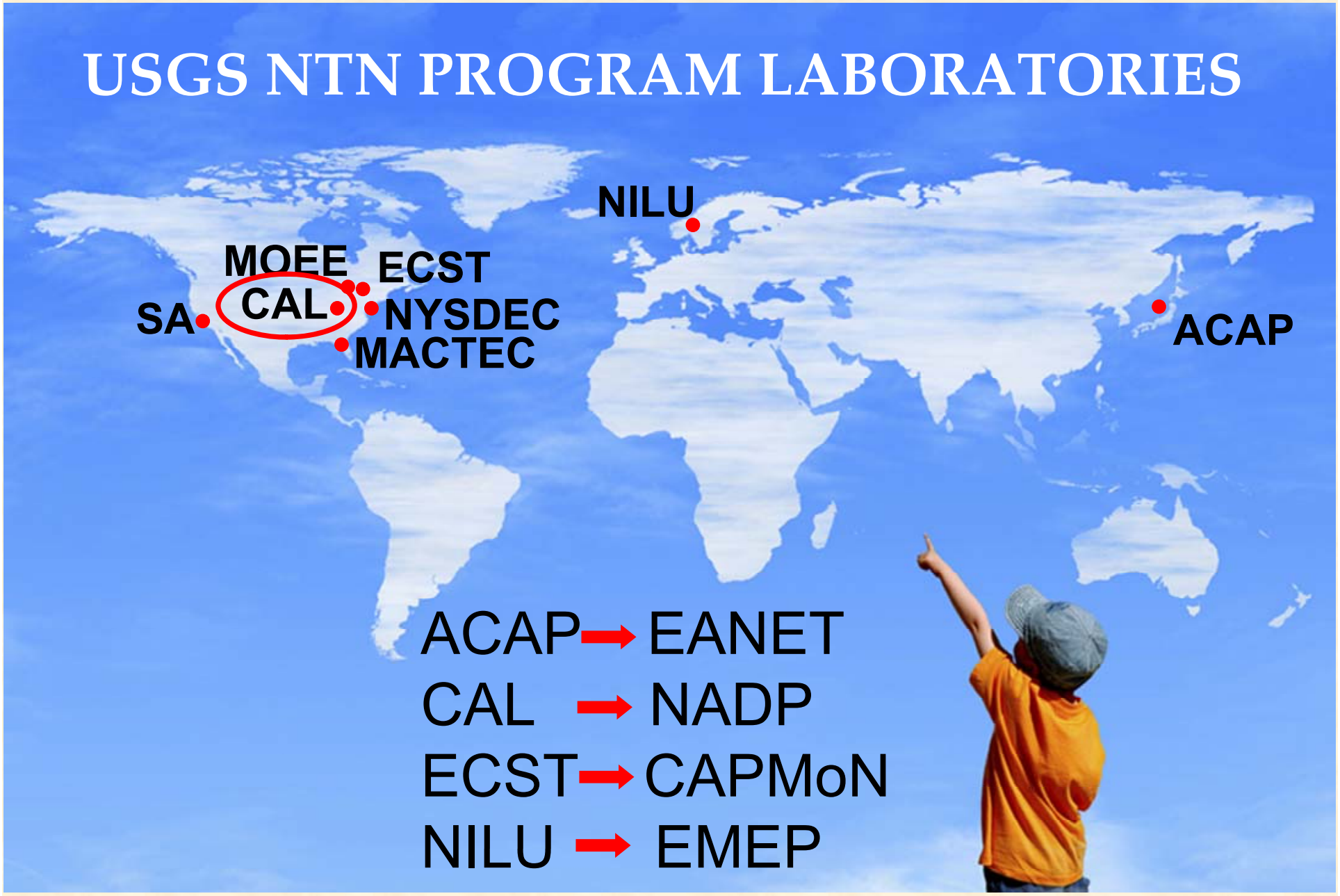
USGS NTN PROGRAM LABORATORIES



ACAP → EANET
CAL → NADP
ECST → CAPMoN
NILU → EMEP

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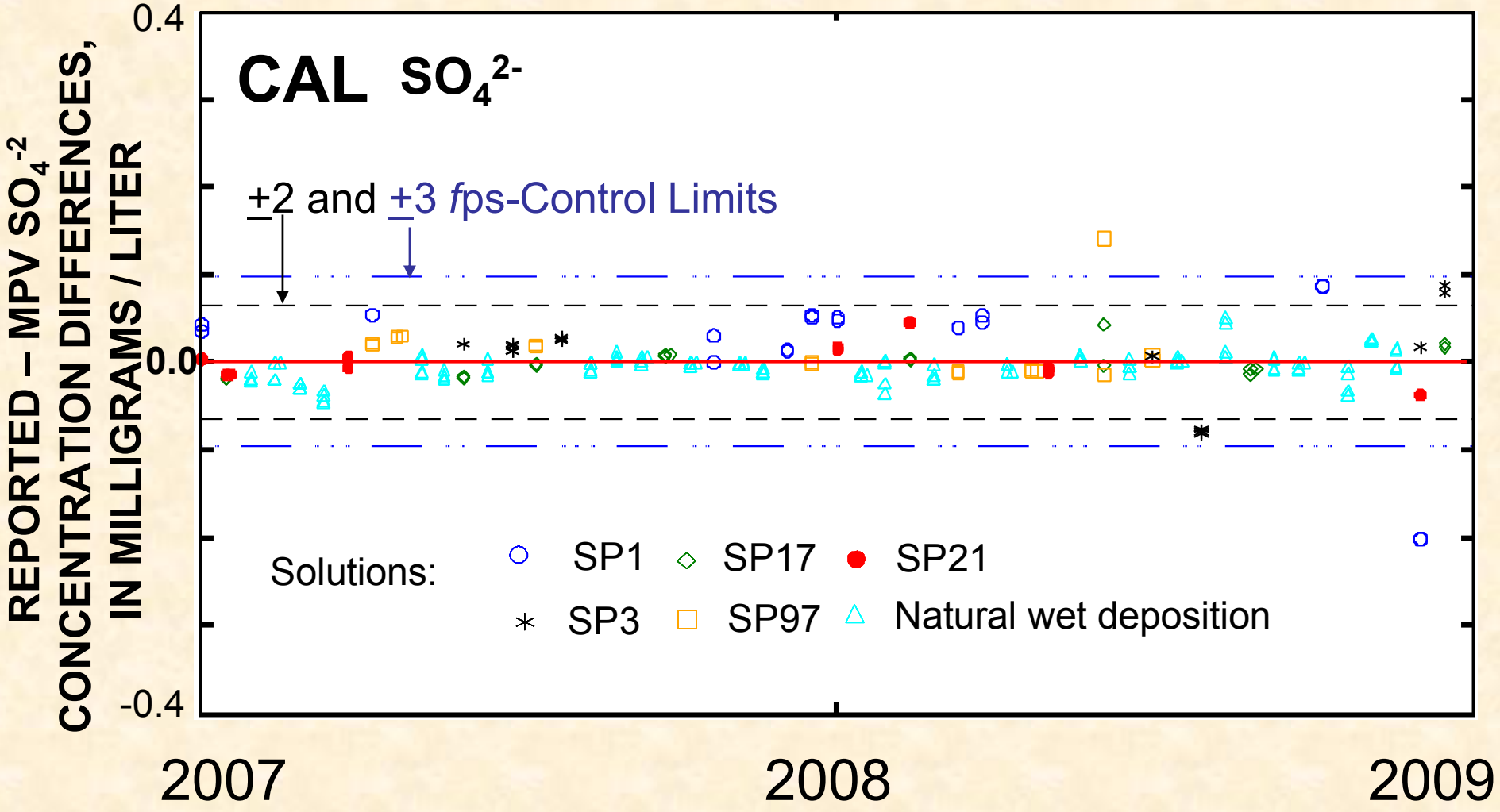

Example Non-Parametric Control Chart for CAL Sulfate

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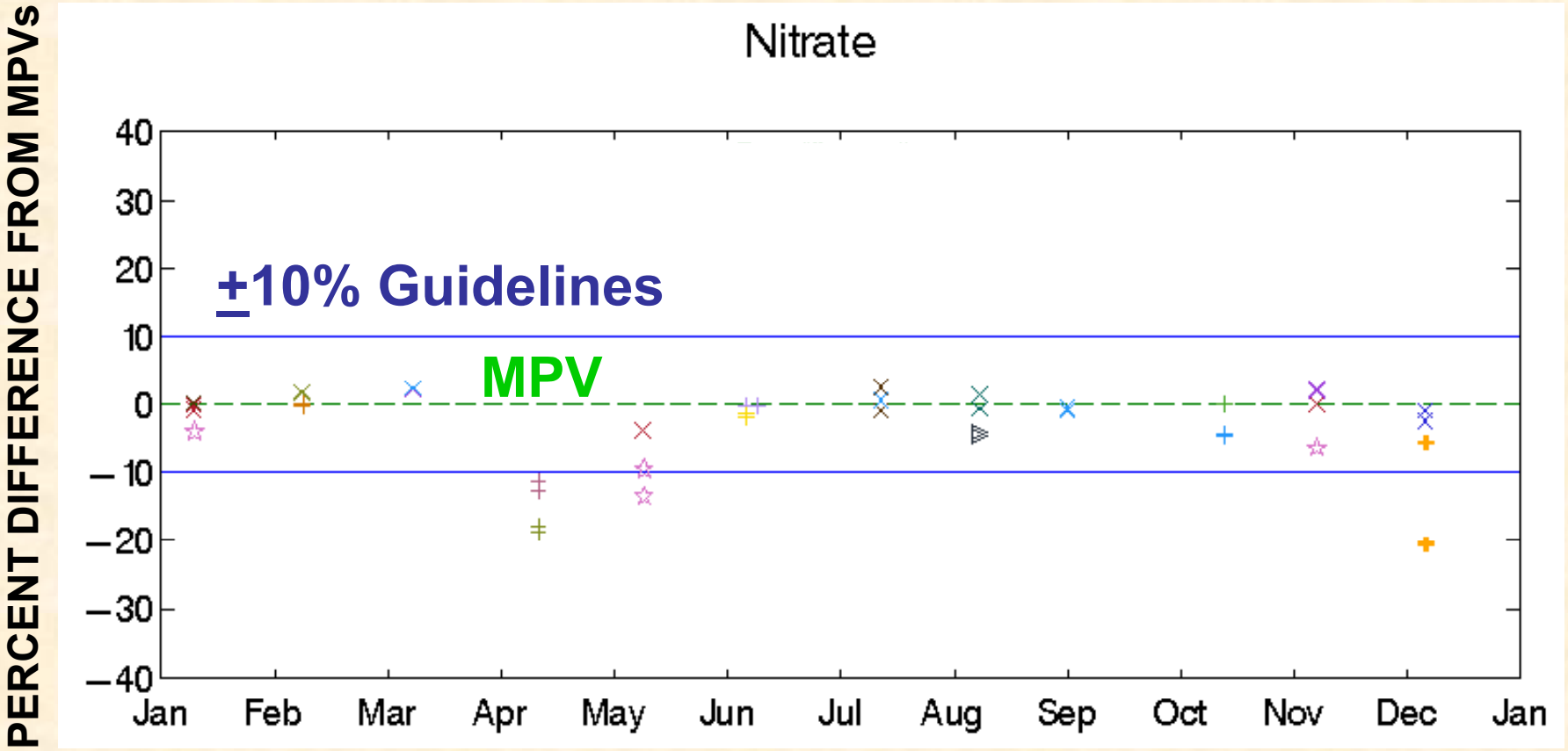
2011 Relative Percent Difference from MPVs
For New York State Dept. Environmental Conservation



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Number of analyses outside +/-10% difference control limits for 3 labs during 2011

Analyte	Laboratory		
	CAL	ECST	AMEC
Ca^{2+}	7	8	3
Mg^{2+}	7	11	6
Na^{+}		5	1
K^{+}	6	10	7
NH_4^{+}	3	6	4
Cl^{-}	2	2	2
NO_3^{-}		1	
SO_4^{2-}			1
H-ion (pH)			
Spec. Cond.	10		

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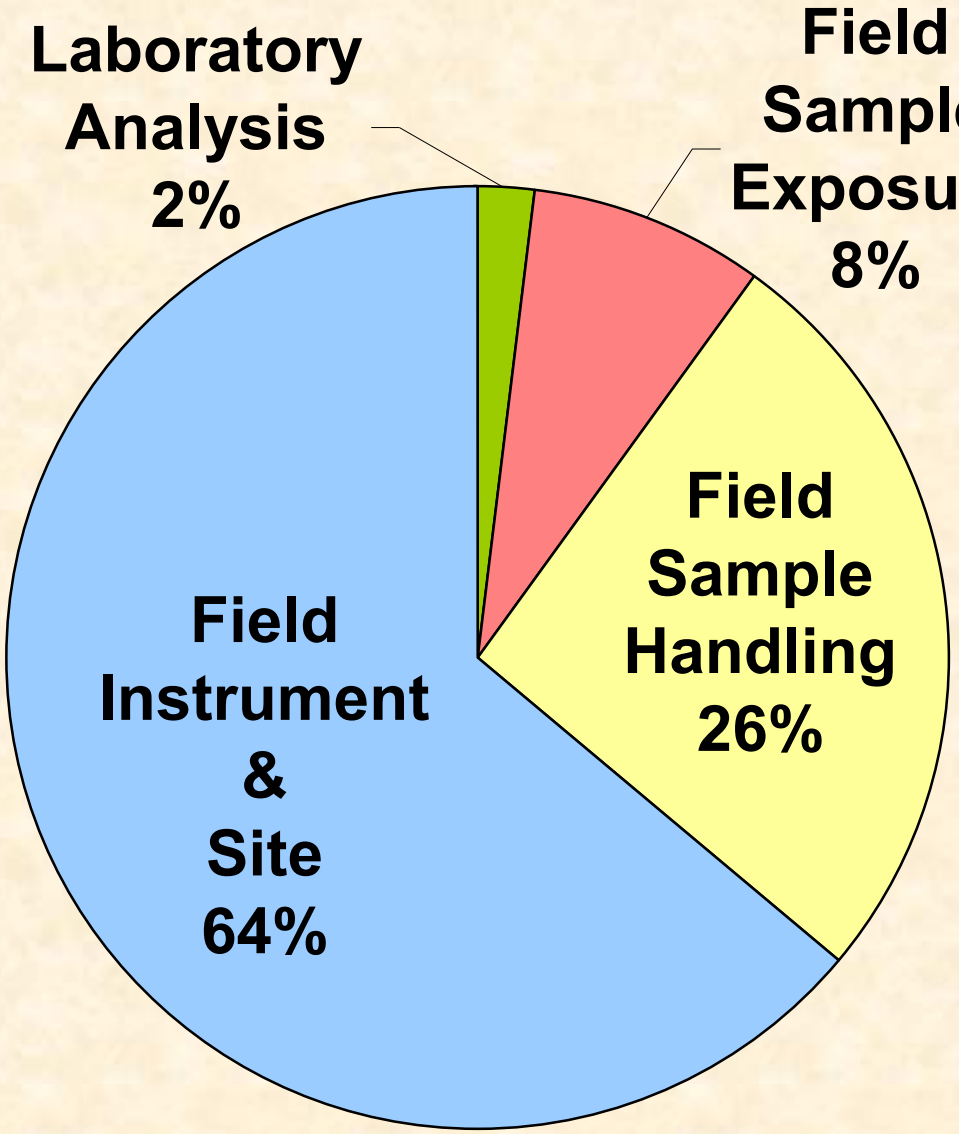
Variability

Wet Deposition Data Variability



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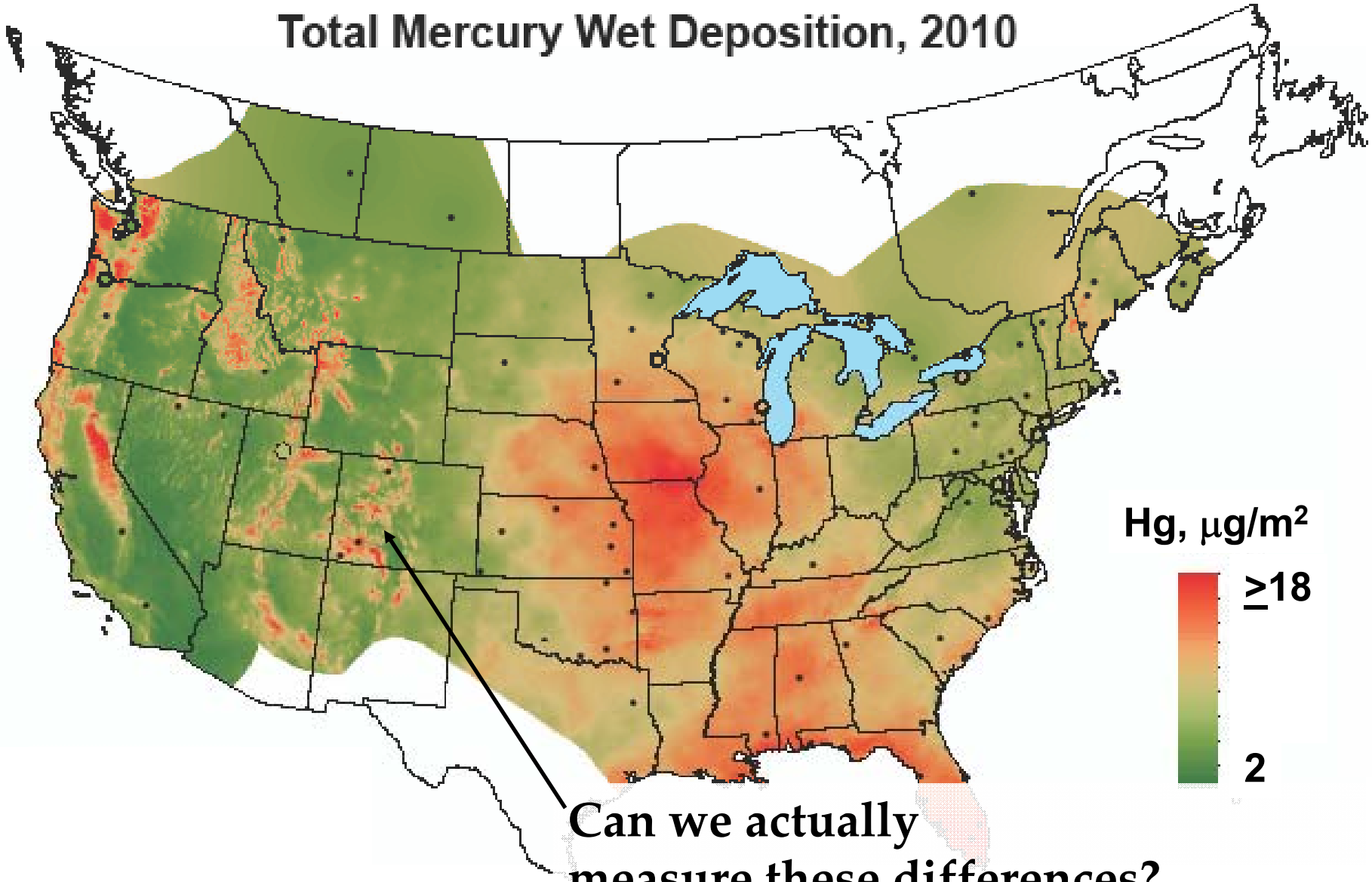
Total Mercury Wet Deposition, 2010
Hg, μg/m²
≥18
2
Can we actually
measure these differences?
How reliable is the interpolation?
National Atmospheric Deposition Program/Mercury Depos
http://nadp.isws.illinois.edu

Common Sources of Wet-Deposition Variability

Collector Fetch / Location – trees, buildings, towers, other nearby objects
(a.k.a. "natural variability")

Field Methods - compliance / non-compliance

Collector Performance – lid sensors & motors

Raingage Performance – Calibrated? Recording properly?

Laboratory Variability – procedures, instruments, contamination

Contamination Variability – climate, landscape, seasonality

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Fetch Differences

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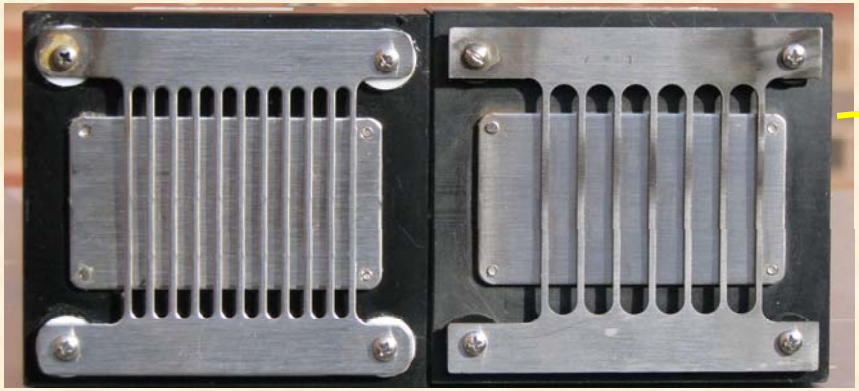
Increased sensitivity can increase variability.

N-CON Optical Sensor
6 particles / 50 sec.



ACM Grid Sensor, >> particles / 50 sec.

Raingage Performance / Seasonal Differences

Snow bridging on gages – an example of conditions that create variability & uncertainty in precipitation records.

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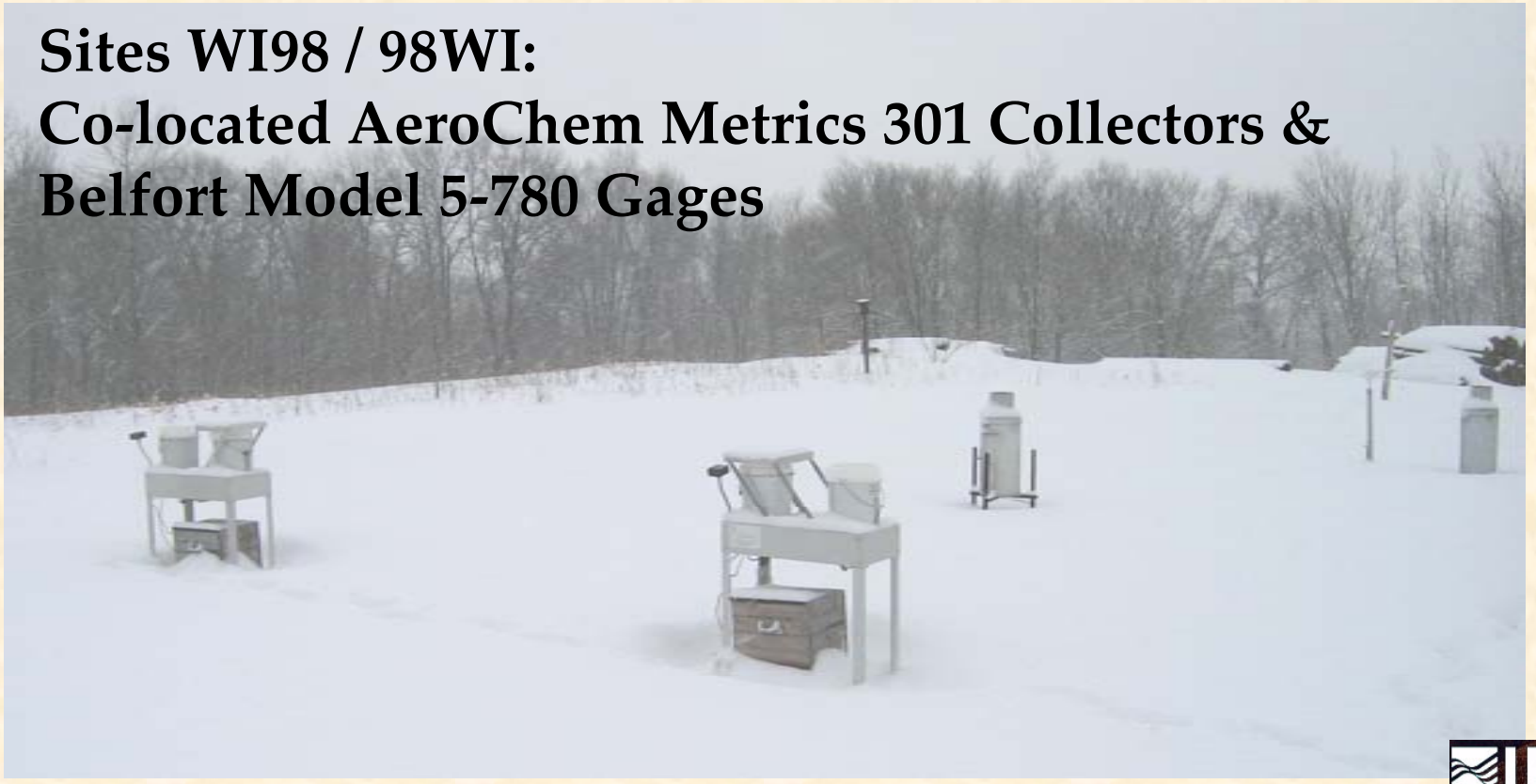
Measure Variability with Replicate Samples

- Concurrent, multiple samples collected at same times, same locations, with identical instruments and protocols.



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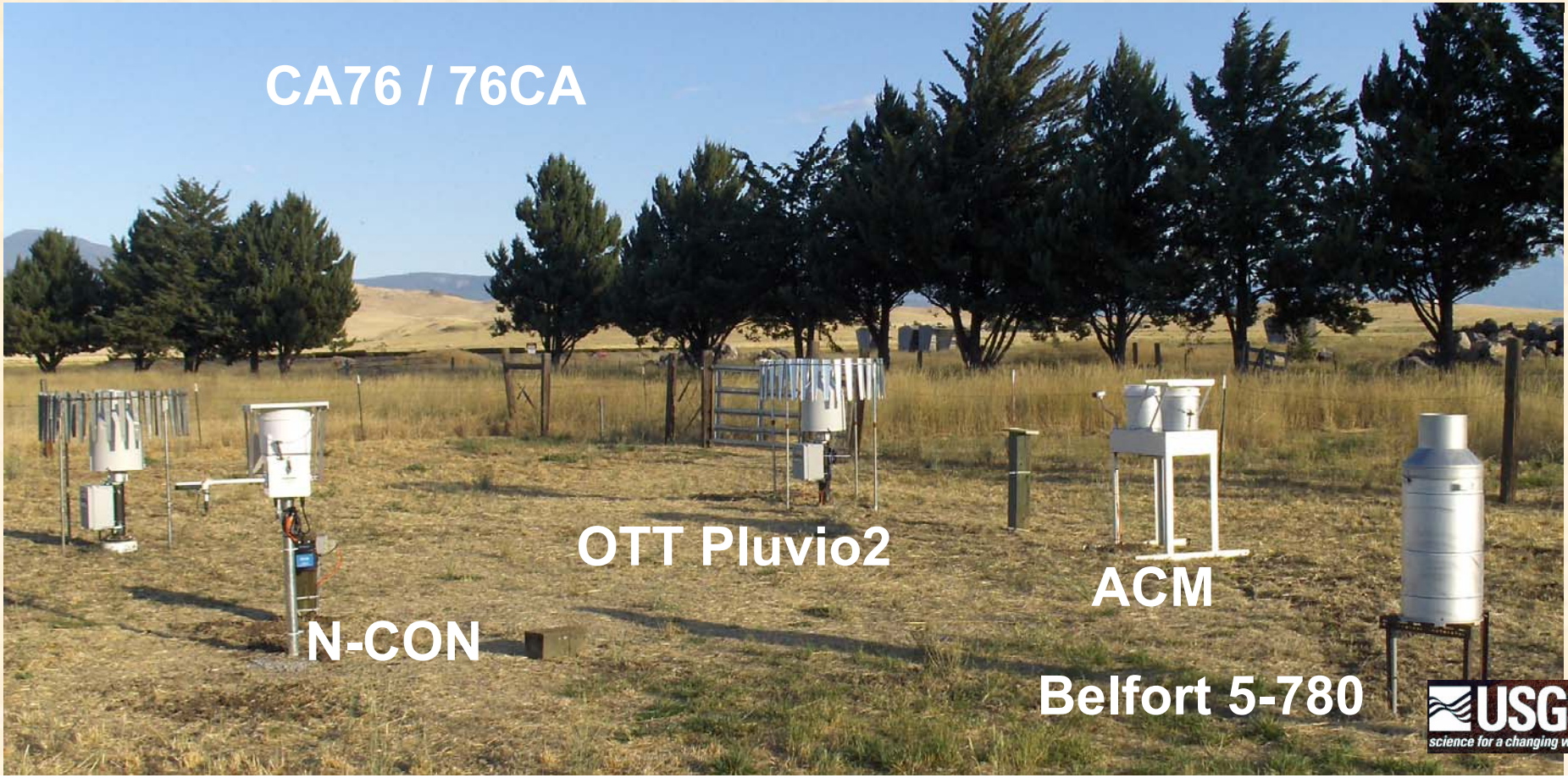
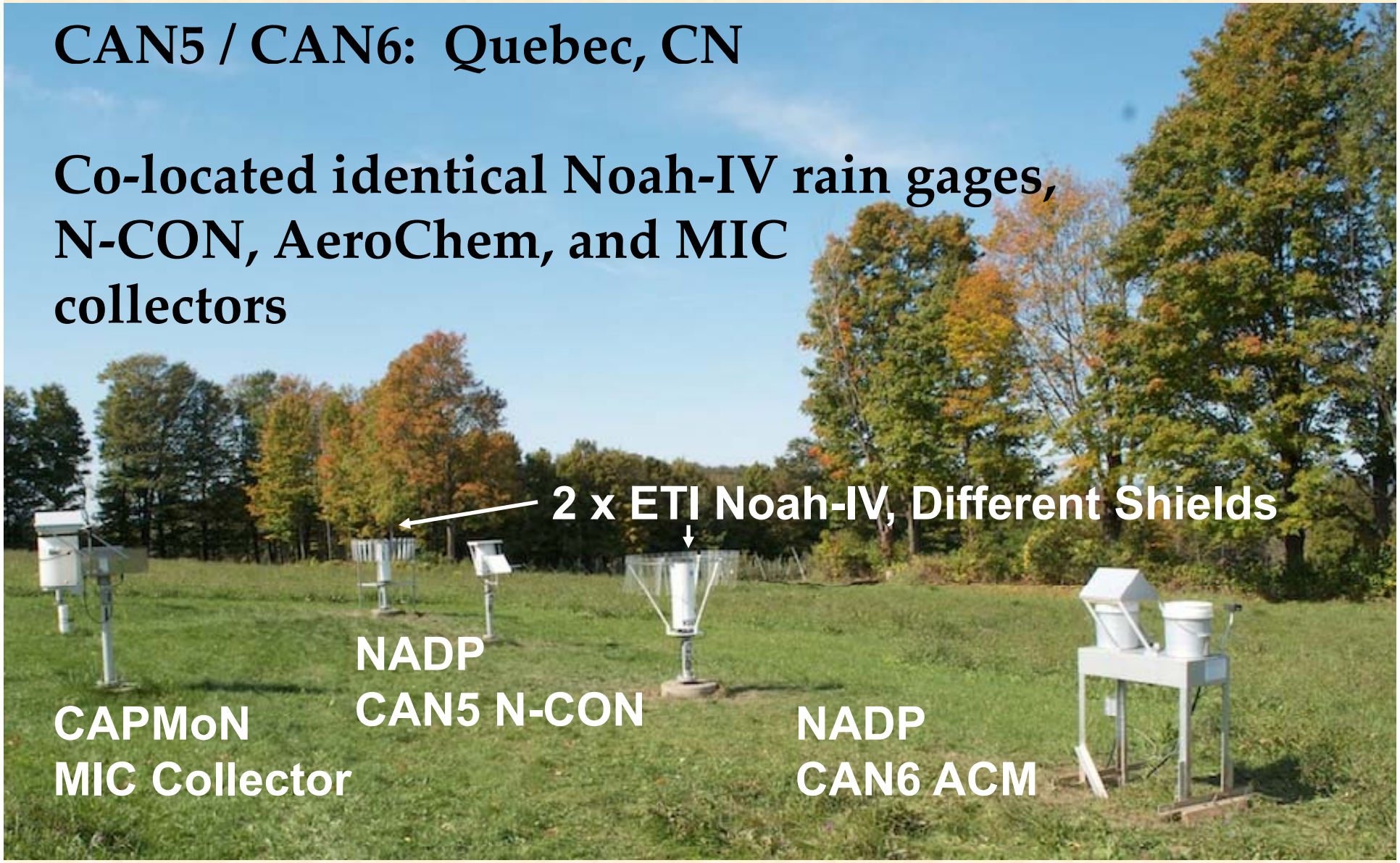
"Non-replicate" Samples

- Concurrent, multiple samples collected at same time, same location, but with different instruments or field protocols.



CAN5 / CAN6: Quebec, CN

Co-located identical Noah-IV rain gages, N-CON, AeroChem, and MIC collectors



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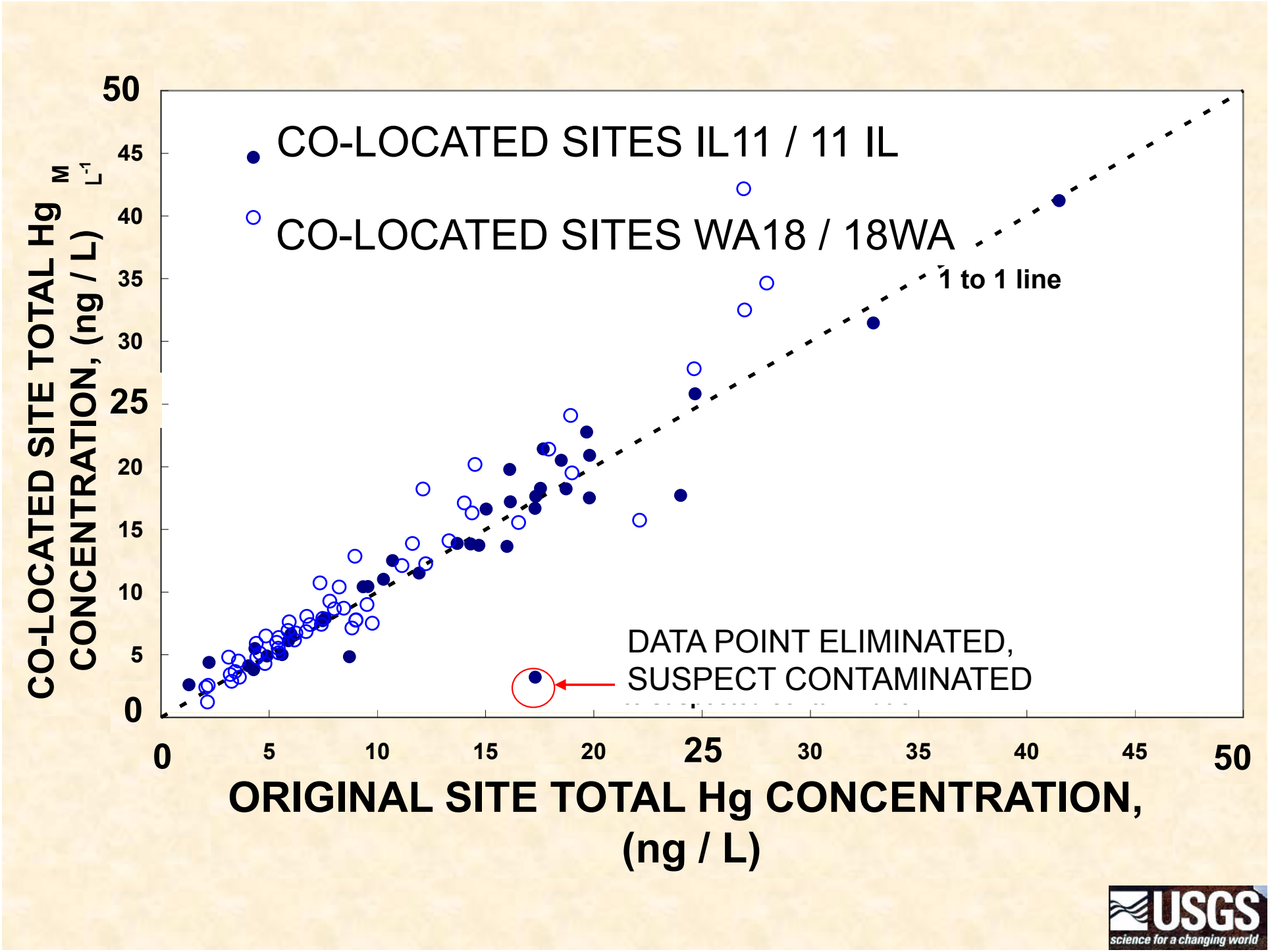
CO-LOCATED SITES IL11 / 11 IL
CO-LOCATED SITES WA18 / 18WA
1 to 1 line
DATA POINT ELIMINATED,
SUSPECT CONTAMINATED
CO-LOCATED SITE TOTAL Hg CONCENTRATION, (ng / L)
ORIGINAL SITE TOTAL Hg CONCENTRATION, (ng / L)
0
5
10
15
20
25
30
35
40
45
50

Minimum Resolvable Difference Estimator m_d

$$m_d = \left(\frac{(1 + Z \bullet RSD_{average})}{(1 - Z \bullet RSD_{average})} \right).$$

$RSD_{average}$ = Average relative standard deviation of all 2-sample replicates (decimal)

Z = 1.96 for 95% Confidence
1.645 for 90% Confidence
1.28 for 80% Confidence

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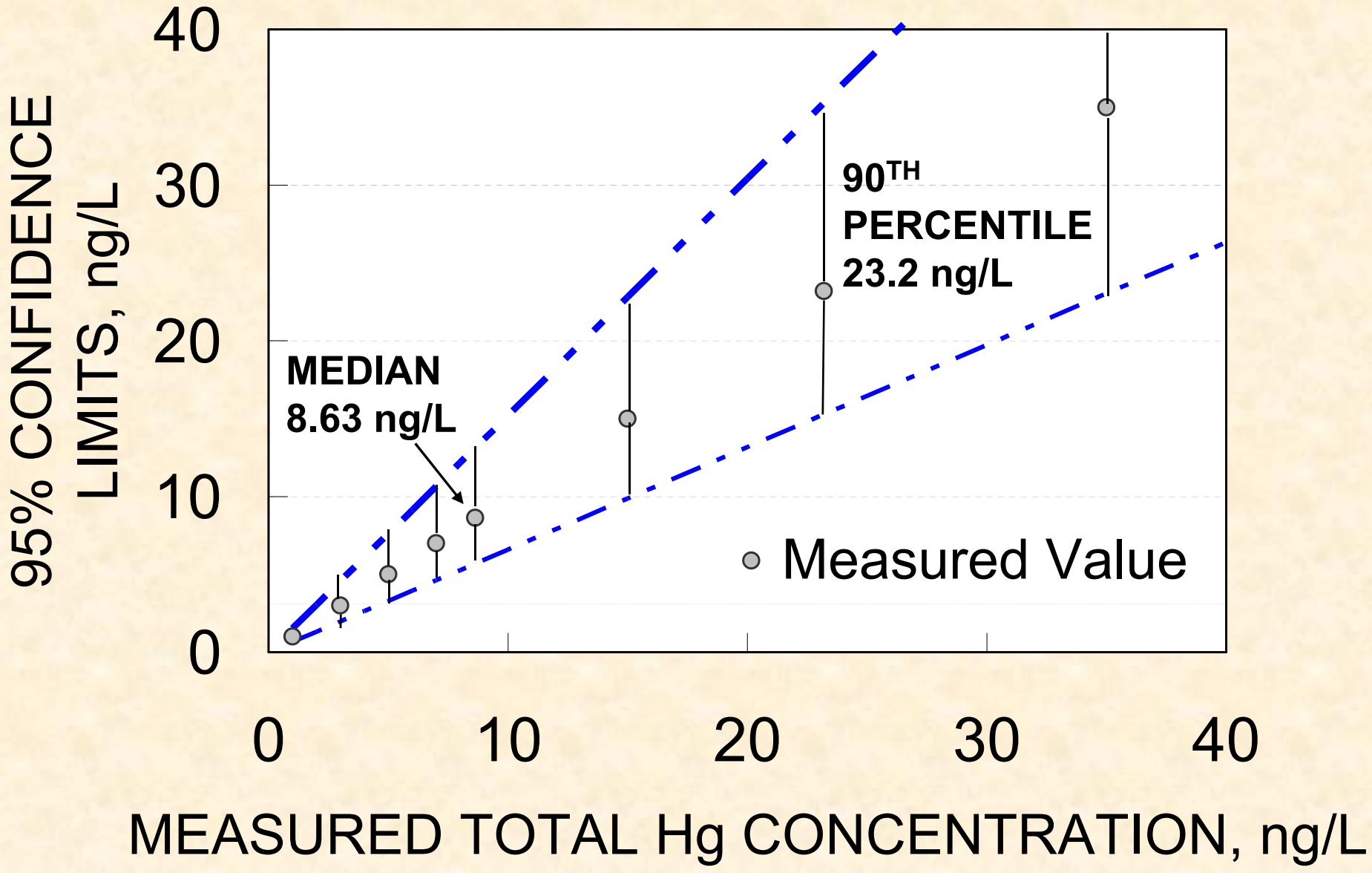
Minimum Resolvable Difference Estimator $\boldsymbol{m_d}$

$\boldsymbol{m_d}$ * C = UCL of Resolution

C ÷ $\boldsymbol{m_d}$ = LCL of Resolution

C = Concentration Measurement



Wetherbee, Gay, Brunette, & Sweet (2007),
Environmental Monitoring and Assessment

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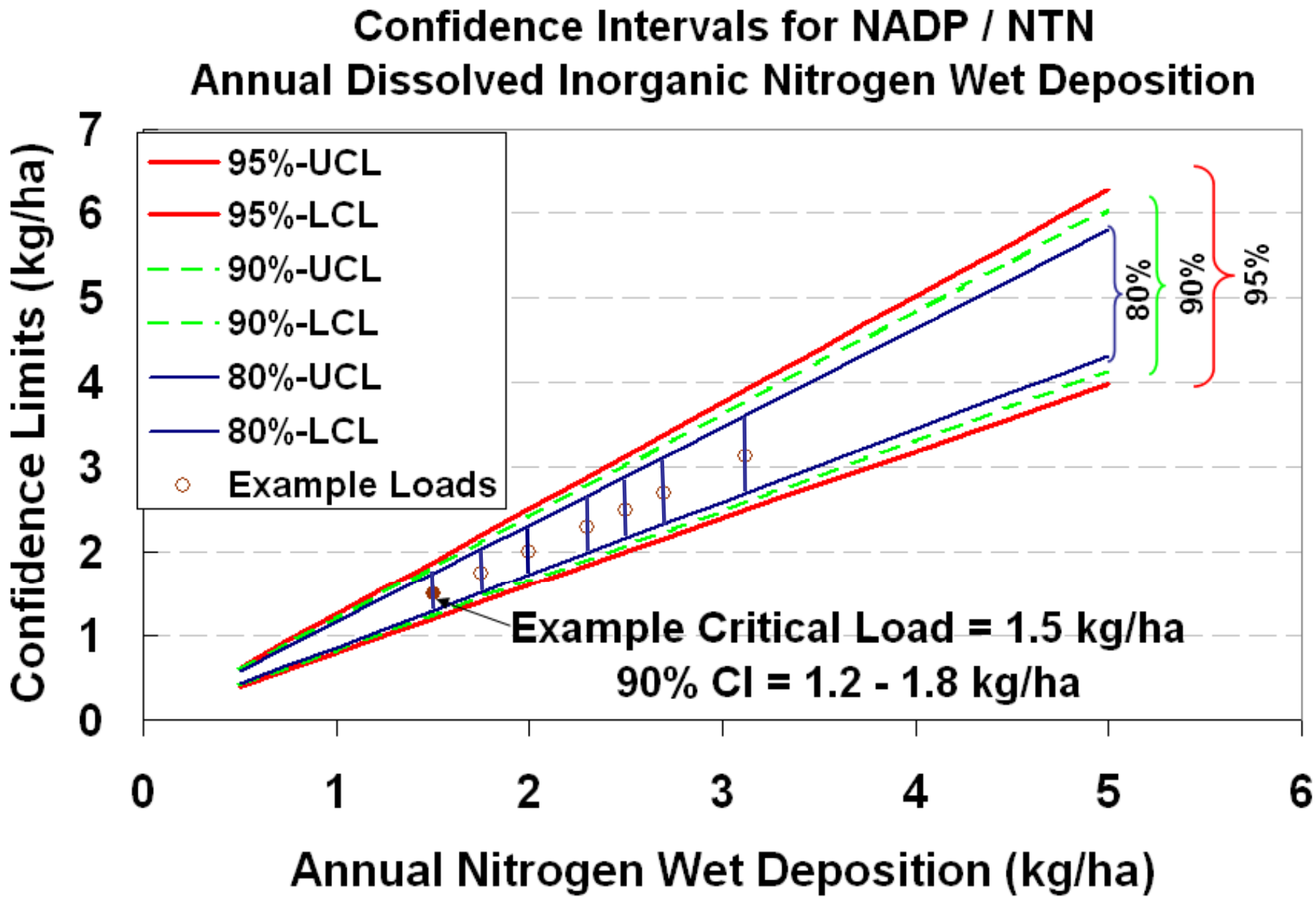
Confidence Intervals for NADP / NTN
Annual Dissolved Inorganic Nitrogen Wet Deposition
Confidence Limits (kg/ha)
Annual Nitrogen Wet Deposition (kg/ha)
95%-UCL
95%-LCL
90%-UCL
90%-LCL
80%-UCL
80%-LCL
Example Loads
80%
90%
95%
Example Critical Load = 1.5 kg/ha
90% CI = 1.2 - 1.8 kg/ha
0
1
2
3
4
5
6
7

NADP Site Surveys
&
Instrument Upgrades

External USEPA Site Survey Program

100 Sites per year visited by audit personnel contracted to USEPA.

Every site visited approximately once every 3 years.

Networks: NTN, AIRMoN, MDN

Audits cover:

- Operator techniques, problems
- Site conditions
- Instrument calibration & performance
- Reports to site sponsors/operators
- Annual report & presentation at annual NADP meetings

EPA United States Environmental Protection Agency

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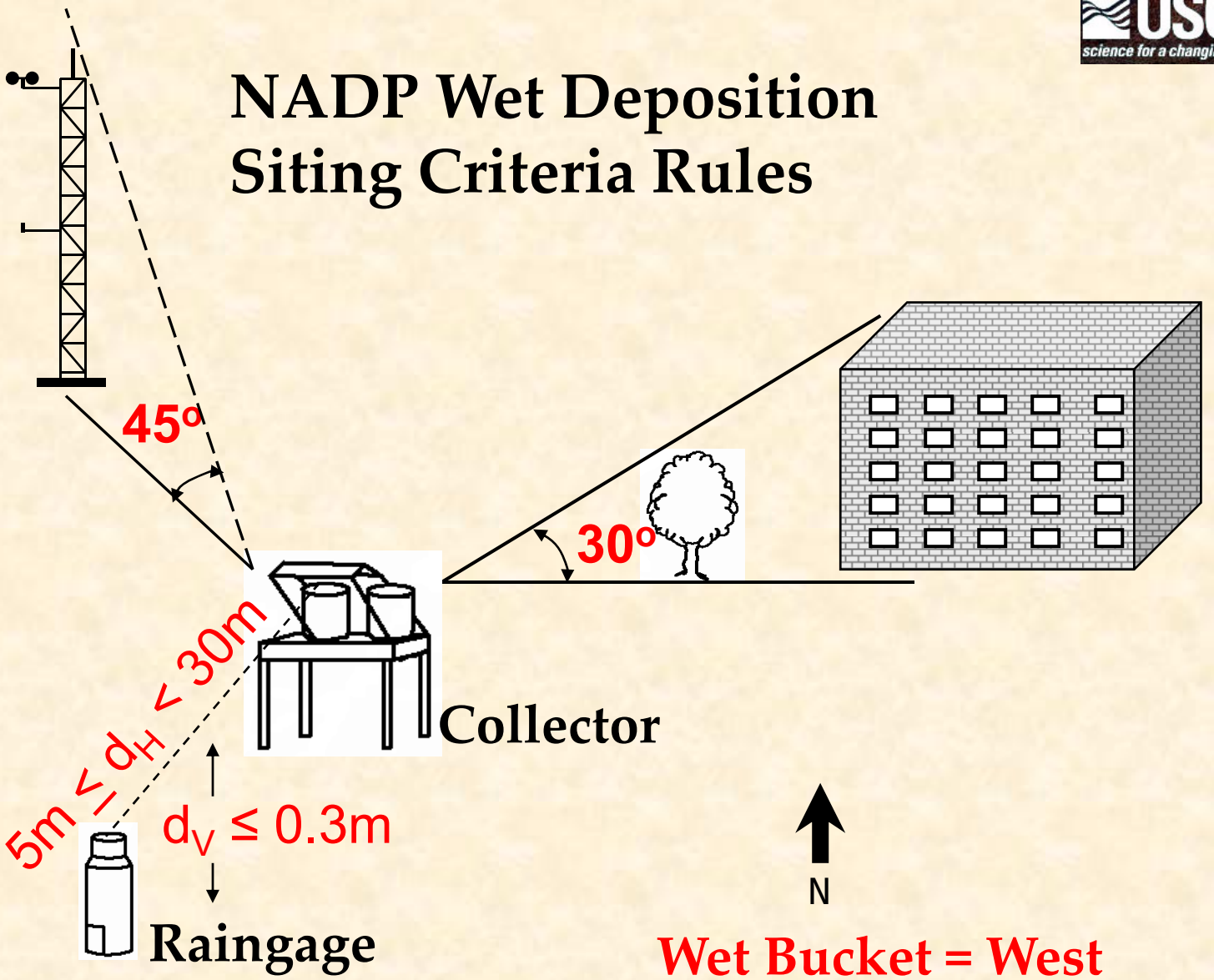
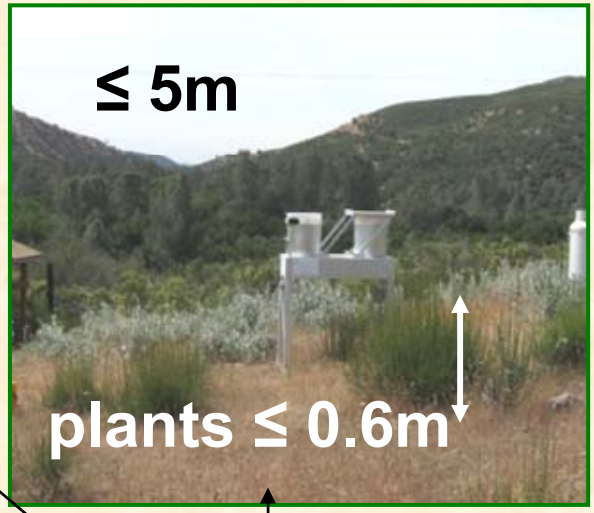
NADP Wet Deposition Siting Criteria Rules

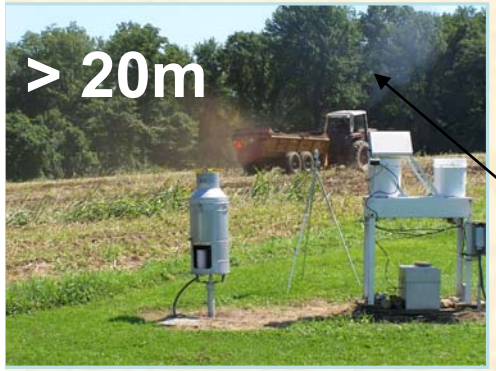


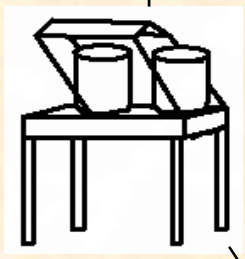
Wet Bucket = West
Sensor = North

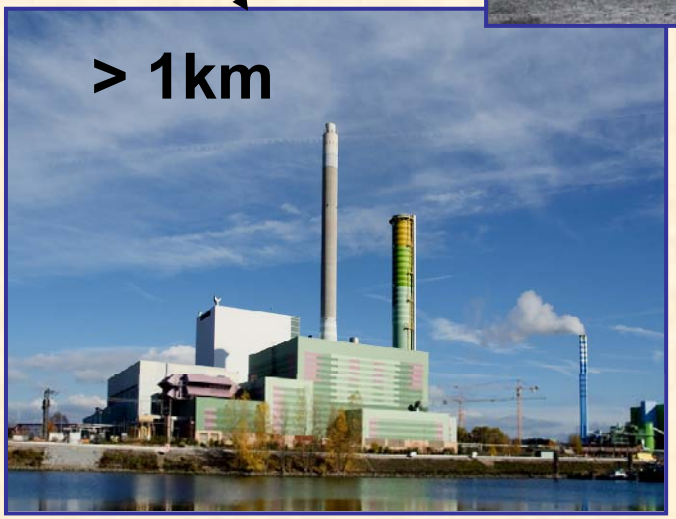
http://nadp.isws.illinois.edu/lib/manuals/NADP_Site_Selection_and_Installation_Manual.pdf

NADP Siting Criteria









USGS
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FL11, 1983

FL11, 2010

USGS
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VA13, 1983

VA13, 2011

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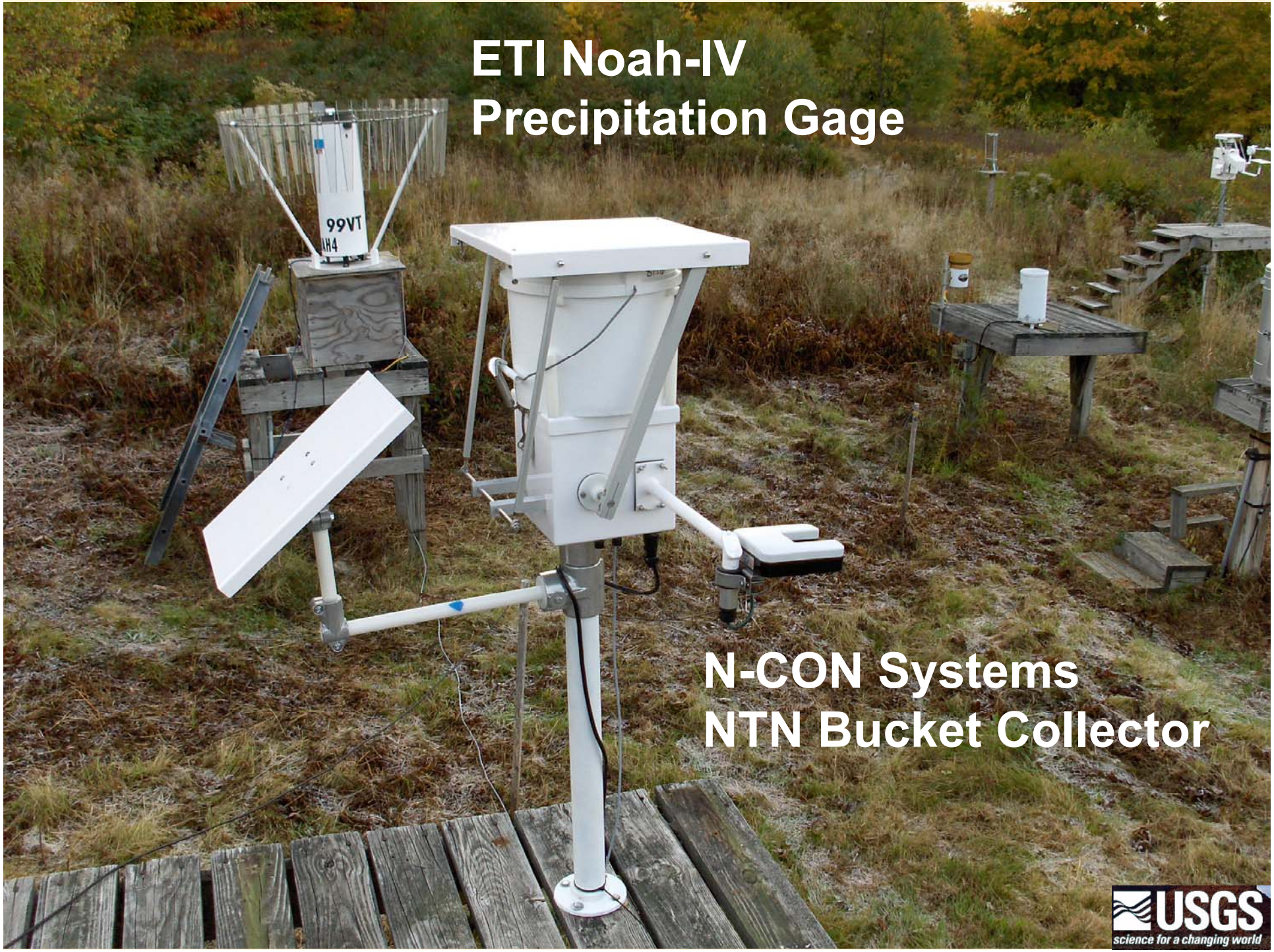
ETI Noah-IV
Precipitation Gage
99VT
LH4
N-CON Systems
NTN Bucket Collector
USGS
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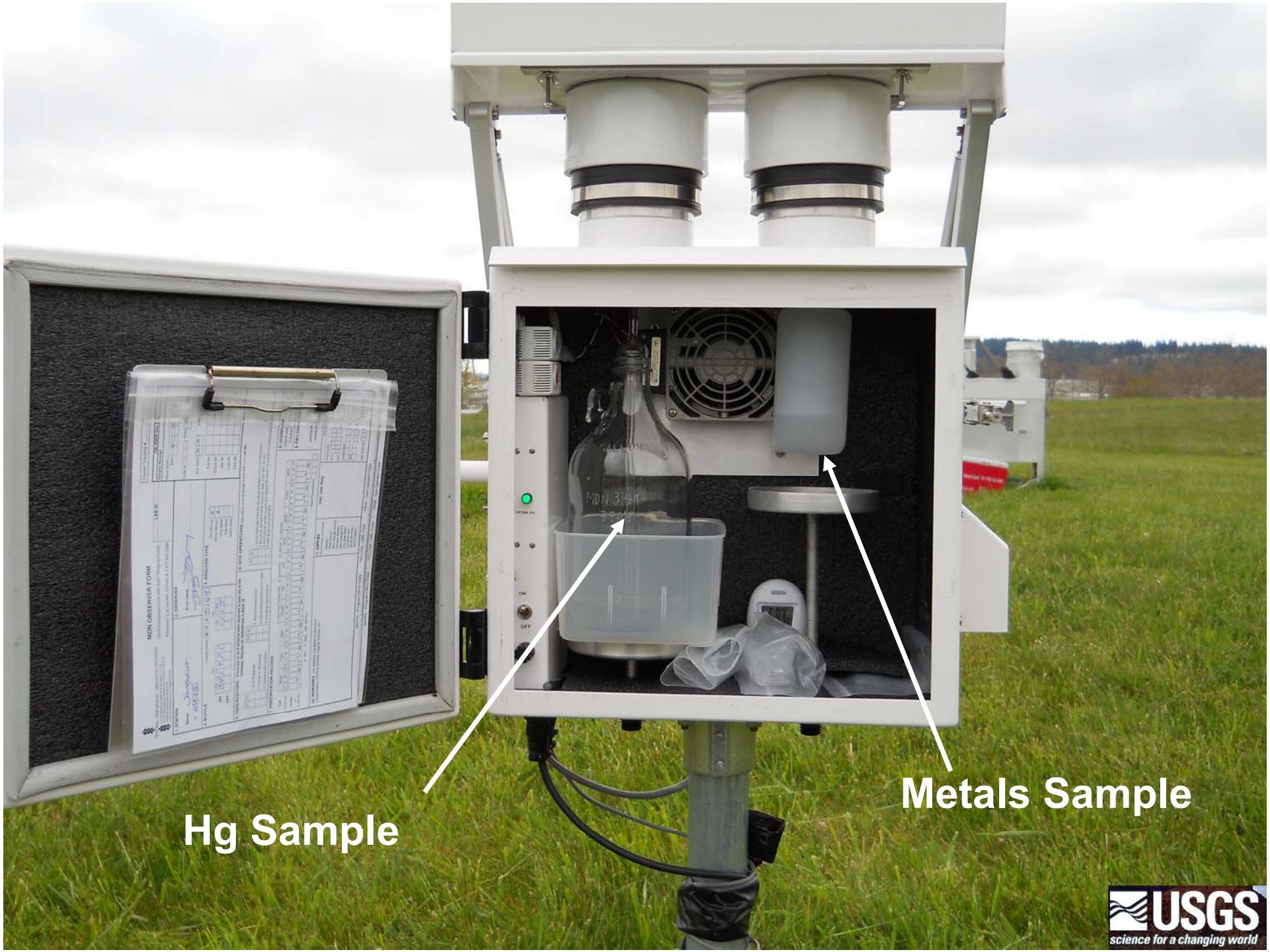
N-CON Systems
Dual Chimney
MDN Collector
USGS
science for a changing world


Hg Sample
Metals Sample
USGS
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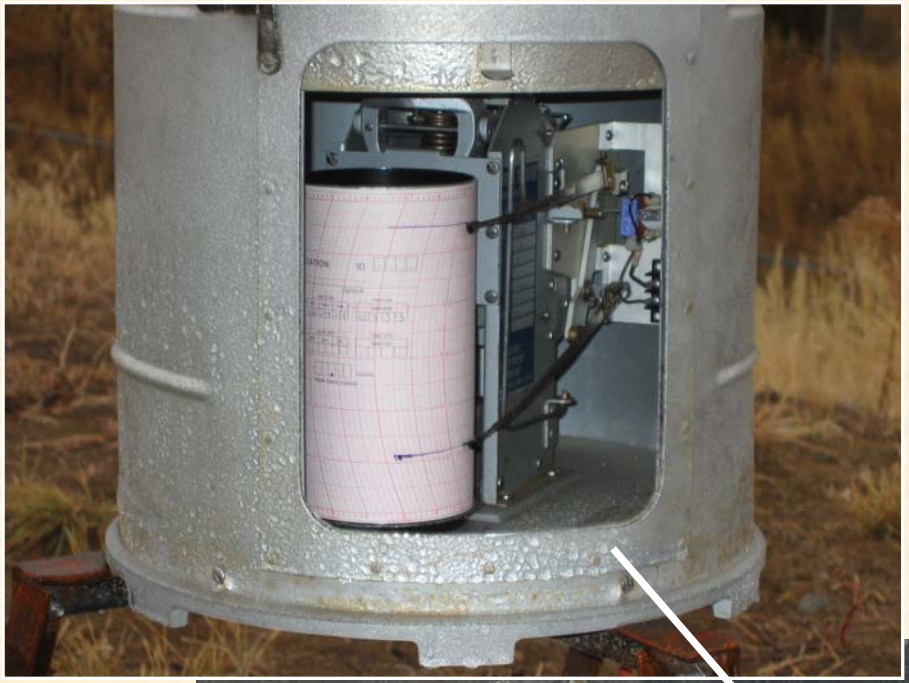
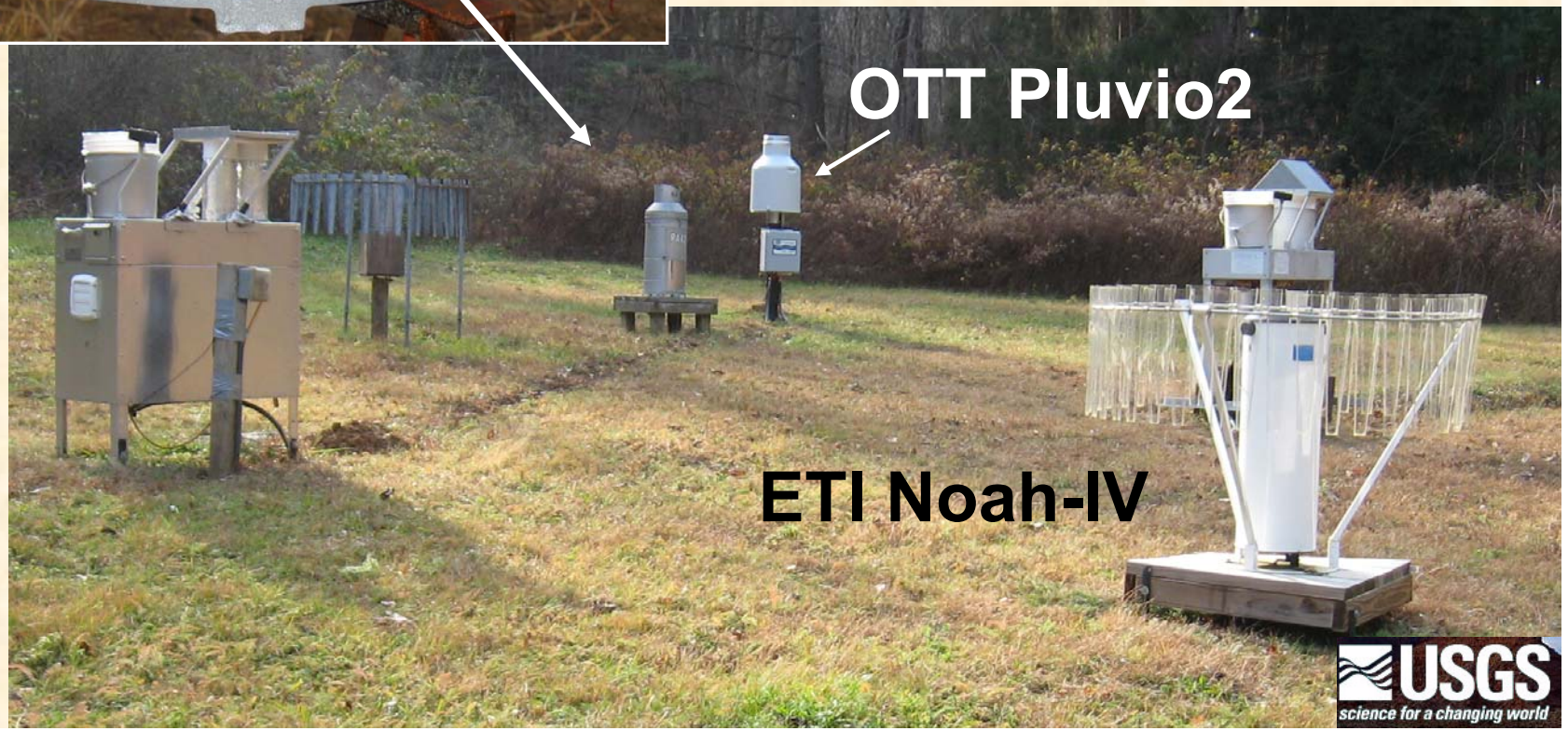
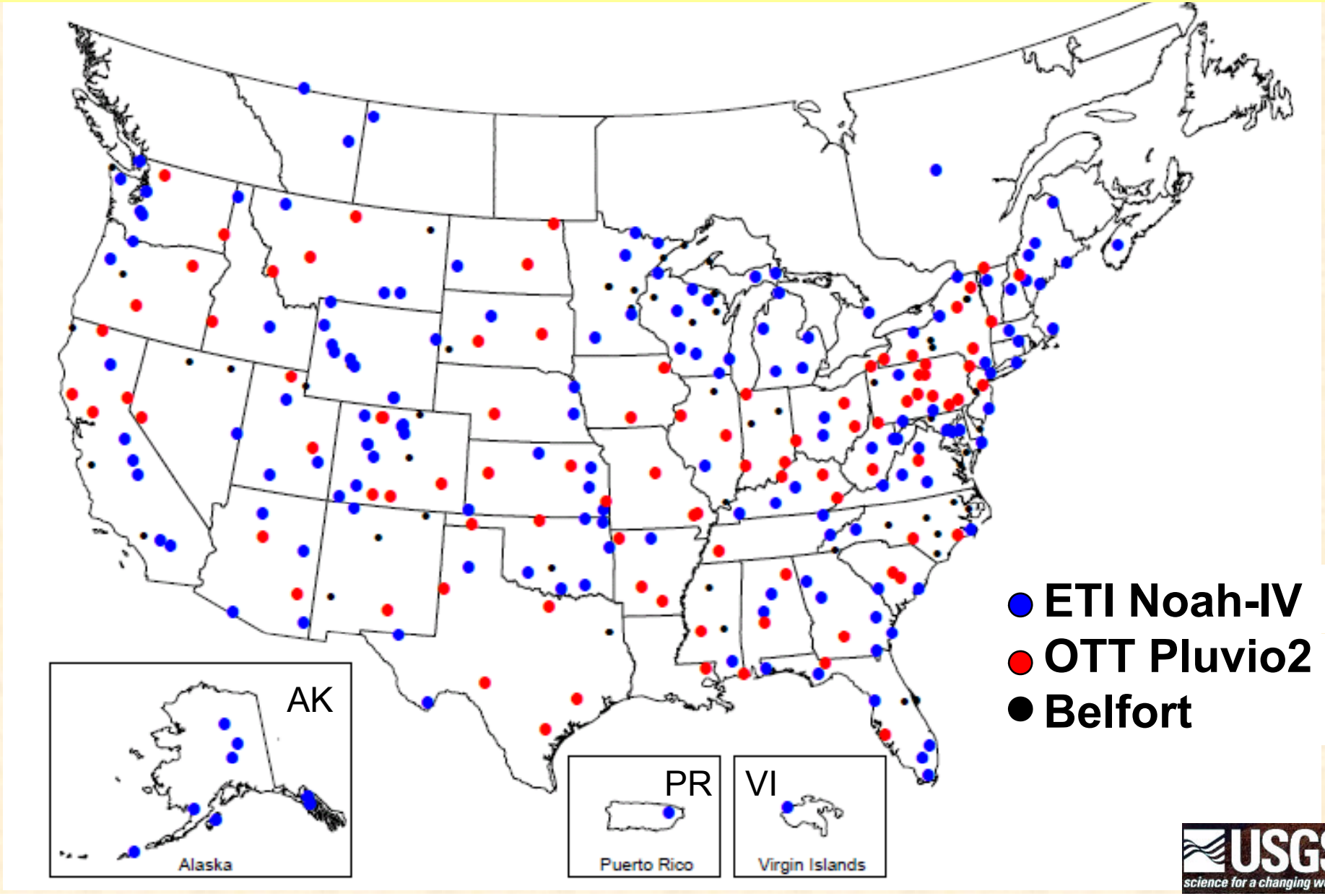


Belfort 5-780
Chart Recording Gage



Current Electronic Raingage Network

(All Networks) ...as of April 2012



Concluding Messages

- Precipitation chemistry data require strict attention to clean and consistent field collection and laboratory analysis protocols.

- QC data are collected to quantify bias and variability of NADP data and provide information to achieve QA goals and objectives.

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Concluding Messages

- QC results provide information to evaluate temporal trends and spatial patterns of wet deposition.

- As NADP upgrades its infrastructure to more modern instruments, QC data are needed to discern between environmental signals and instrument bias.

- NADP now has a number of spare Belfort 5-780 raingages and AeroChem Metrics 301 collectors that could be used for monitoring in USA and abroad.

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