



# Statistical Limitations of Disinfectant Residual Measurements

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# Background

- We do not know with any certainty the concentration of disinfectant residual that is ***Detectable*** and ***Effective***, much less what is ***Protective***
- Studies clearly indicate that residual disinfectant alone is not a sufficient indicator of water quality in distribution systems or health risks for customers
- The current PA DEP minimum disinfectant residual concentration – 0.02 mg/L – is based on a method detection limit and is not appropriate as a reporting limit
- The proposed PA DEP revisions to rules on secondary disinfection are intended to ensure that data it is collecting and recording are legitimate data

# Overview

## **Uncertainty and variability of residual measurement are critical context for minimum residual levels**

- A large-scale study of residual measurement in CO waters, Hach studies & studies by PA utilities all indicate that chlorine residual is detectable around 0.09 mg/L. This level accounts for
  - Interferences
  - Bias
  - Inter-laboratory variability
- We cannot measure disinfectant residual to an accuracy of hundredths of mg/L (0.00). Regulatory minimum residual levels should reflect this reality
- Variability and uncertainty in residual concentrations necessitate distribution system operating levels significantly above a minimum residual level

# Outline

- Regulations for minimum secondary disinfectant concentration
  - Current federal standards
  - States' standards
- The meaning of “detectable”
  - Agreement – 0.02 mg/L is an unworkable definition of detectable
  - Outline of alternative approaches
  - Support for a detectable residual around 0.1 mg/L
- Measurement precision and implications for a defensible minimum residual level
  - Assessing compliance
  - Operating levels v. regulatory levels
- Conclusions and Discussion
  - Reinforcing the messages
  - Science and the regulatory process

Minimum disinfectant residual and its regulation

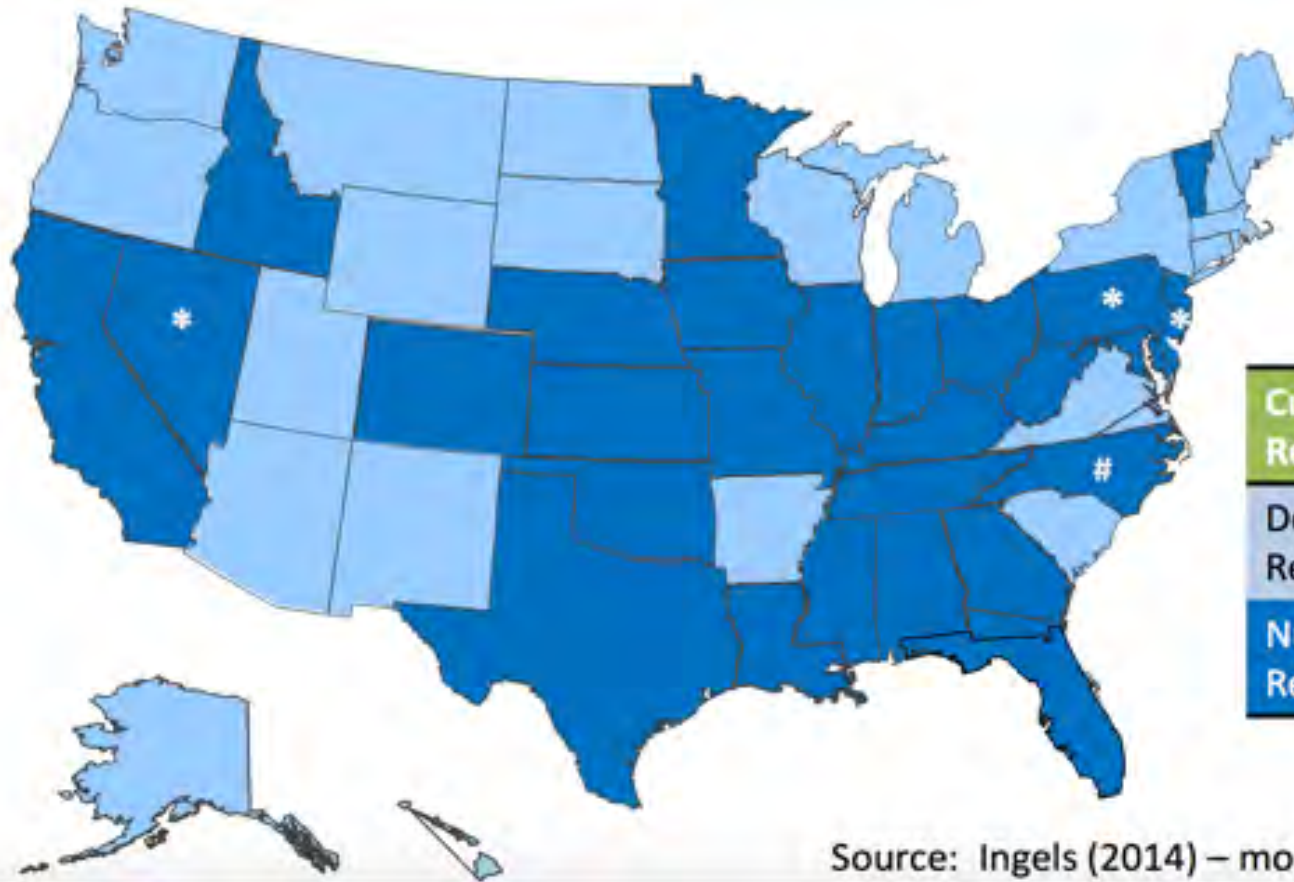
# BACKGROUND

# Overview of Regulations

- Federal Regulations
  - Must have detectable residual in 95% of samples collected each month; ***definition of detectable left to the states***
  - HPC < 500 is an alternate indication of detectable residual
- States' approaches
  - Minimum residual concentrations range from “detectable” without a specific definition to 1.5 mg/L
  - “At all locations” v. 95% of samples
  - In most cases no clear indication of the basis for States' choices (Notable exception is Colorado)

# Secondary Disinfection Regulations - Nationwide

Diversity of state approaches reflects unsettled science



Current Requirement	# of States
Detectable Residual	22
Numeric Minimum Residual	28

Source: Ingels (2014) – modified and updated

\* = Numerical standard < 0.2 mg/l

# = Numerical standard is to total chlorine

Agreement – 0.02 mg/L is an unworkable definition of detectable  
Outline of alternative approaches  
Support for a detectable residual around 0.15 mg/L

# THE MEANING OF DETECTABLE



# 0.02 mg/L is a Poor Measure for Detectable Residual

- 0.02 mg/L is a MDL established in laboratory studies, not a reporting level
- Instruments report concentrations below established detection limits; analysts might take those results seriously
- Many nuances of measuring disinfectant residual result in significant uncertainty and variability
  - Inter-lab differences, inter-analyst difference, differences between instruments, interferences, and actual variability
- Even if it were real, a 0.02 mg/L residual might not indicate that there is an effective disinfectant present (interferences)

# Attempts to Define Detectable

Detectable Concentration	Study or Source	Basis and notes
0.09 mg/L (free or total)	Colorado Department of Public Health and Environment	Statistical analysis of results of samples taken from distribution systems in CO. Accounts for interferences & inter-laboratory differences.
“Detectable” is a research question	Wahman and Pressman [USEPA] (2015)	Review of the literature indicates that organic chloramines may dominate at very low total chlorine concentration.
0.1 mg/L (free or total)	Hach	$0.03^a \text{ mg/L} \times 3.18^b \approx 0.1 \text{ mg/L}$ (95 <sup>th</sup> %ile estimate of the DL based on Hach studies)
0.2 mg/L (free or total)	PA DEP	0.1 mg/L → 0.2 mg/L (adds conservatism to account for interferences, additional uncertainty)

<sup>a</sup> Hach detection limit (laboratory setting)

<sup>b</sup> 99<sup>th</sup> percentile t-distribution statistic for 6 degrees of freedom

# Colorado Department of Public Health and Environment Residual Measurement Study

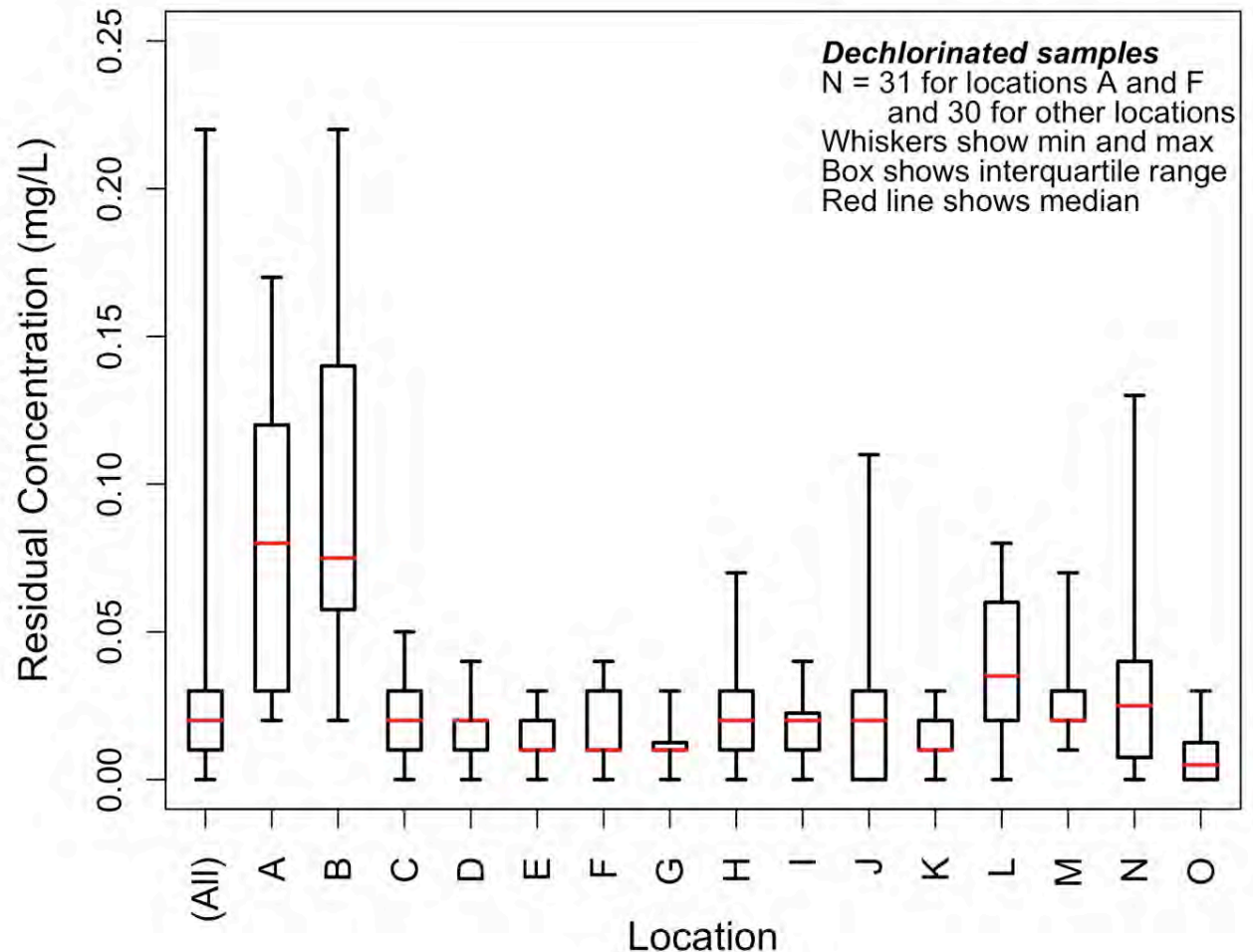
**Goal:** Understand the measurement errors in drinking water samples that did not have a residual

## **Four waters were tested:**

- 1) Water from PWS
- 2) Water from PWS with dechlorinating agent
- 3) Deionized water
- 4) Water from PWS which does not add chemical disinfectant

# CO Study – Dechlorinated Samples

- Non-zero residual measured in most dechlorinated samples
- High variability among replicates for a given location
- Two locations (A and B) deemed to be problematic



# CO Conclusions on “Detectable”

- Concentration data for dechlorinated samples excluding two locations (A and B) were fit to a distribution and the 99<sup>th</sup> percentile value of concentration was estimated
- Result: A measurement above 0.08 mg/L has a ***low probability of falsely indicating a detectable residual***
- Recommendations
  - Method detection limit (MDL) = 0.09 mg/L
  - Based on the MDL and occurrence of *E. coli* and total coliforms when residual disinfectant concentration is less than 0.15 mg/L, CO selected a minimum residual of 0.2 mg/L

Assessing compliance

Operating levels v. regulatory levels

**MEASUREMENT PRECISION AND IMPLICATIONS  
FOR A DEFENSIBLE MINIMUM RESIDUAL LEVEL  
ASSESSING COMPLIANCE  
OPERATING LEVELS V. REGULATORY LEVELS**

# Aqua and PW Lab Studies

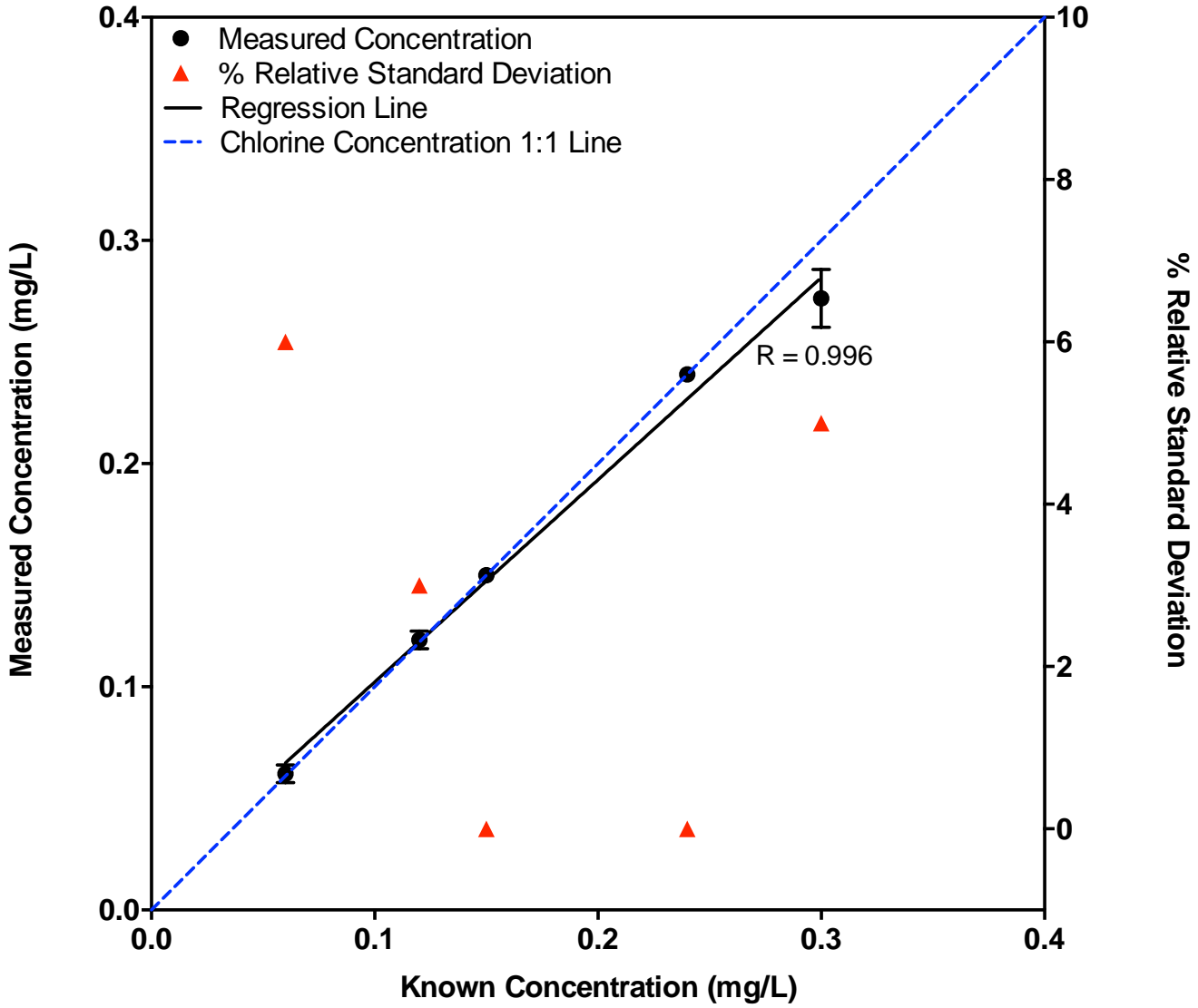
## Objective

- Determine variability in residual measurements to determine whether a 0.20 mg/L (two decimal places) minimum residual is supported
- Quantify uncertainty in the vicinity of the minimum disinfectant concentration

## Methodology

- Replicate measurements of known concentration were performed using
  - Hach DPD Method (PW & Aqua) and
  - Amperometric Titration (only PW)
- All samples were diluted from a stock using deionized water
- Highly skilled analysts conducted measurements on standards between 0 and 0.65 mg/L

# Philadelphia Water – Hach DPD Method

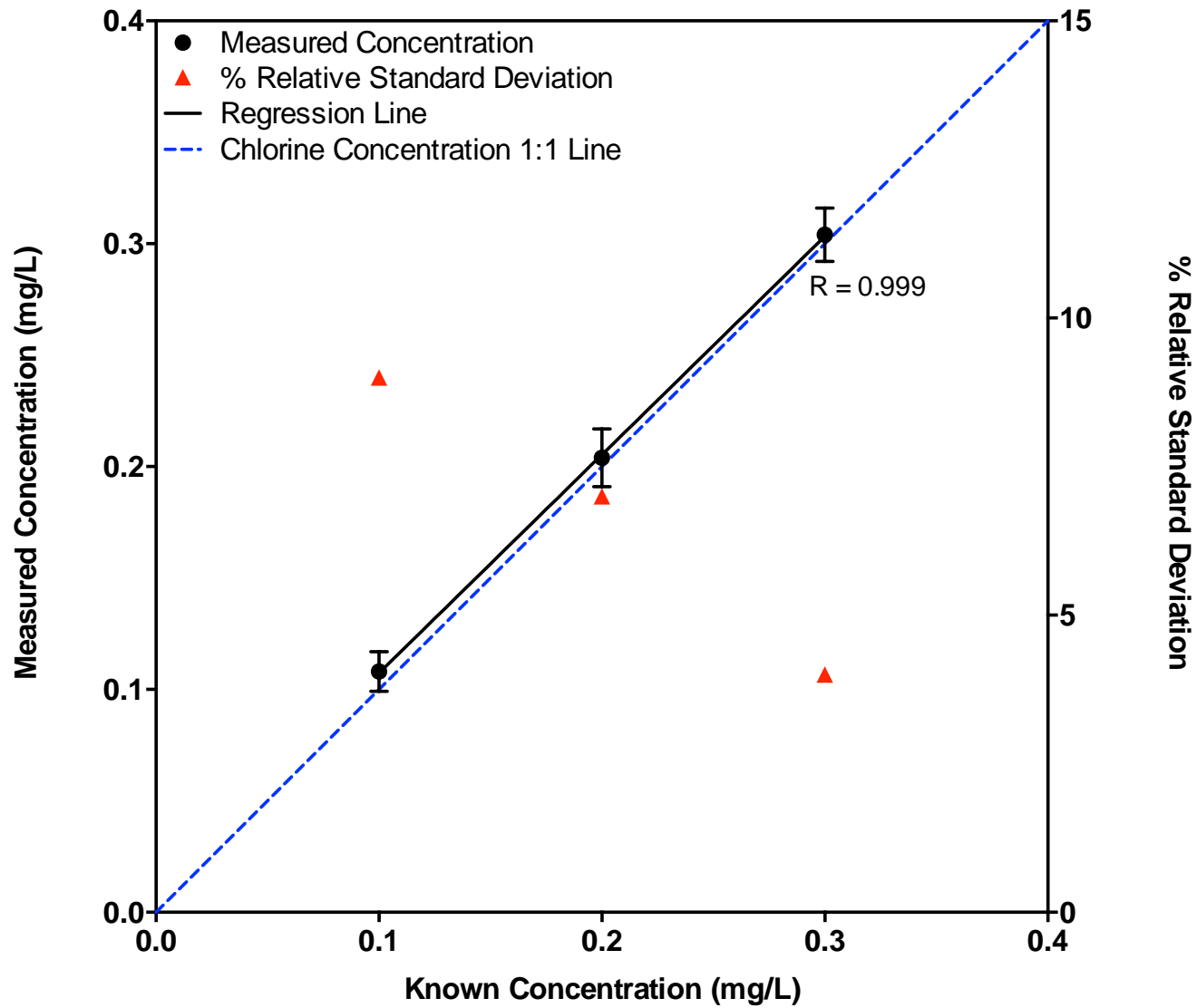


Relative standard deviation (RSD) (aka coefficient of variation, CV) is

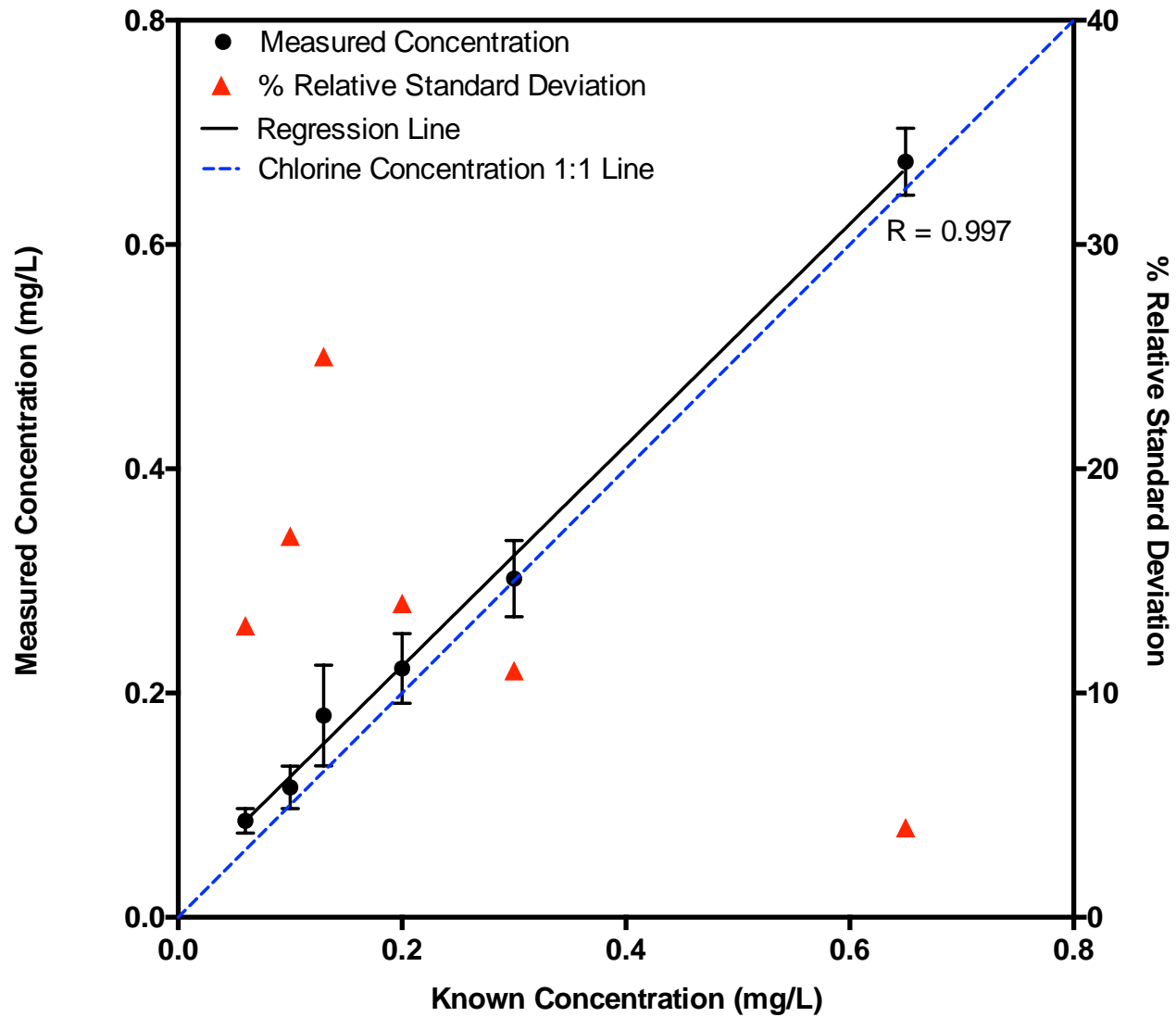
$$\frac{\text{standard deviation}}{\text{mean}} \times 100\%$$



# Philadelphia Water – Amperometric Method



# Aqua America Results-Hach DPD Method



# Aqua America Results-Hach DPD Method

- The average measured chlorine concentration was
  - statistically higher than the known concentration for known concentrations between 0.06 – 0.2 mg/L
  - not statistically different from the known concentration for concentrations above 0.3 mg/L (0.3-0.65 mg/L)
- For locations retained in the CO study, the range of relative standard deviations of residual measurements was
  - 4.6% to 12.7% for dechlorinated samples
  - 20% to greater than 300% for samples that were not dechlorinated
- Relative standard deviation for Aqua experiments conducted at 0.2 mg/L was 15%

# Aqua and PW Results Correspond to a Best-Case Scenario...

- Very well-controlled study:
  - Laboratory grade water used for dilutions
  - Highly trained technicians
- Results provide a lower bound estimate for variability;
- Variability is likely to be higher if tests were performed by other analysts using matrix water

# Operational Implications

- In order to ensure that the measured residual concentration is at least 0.2 mg/L 95% of the time, the minimum operating concentration would have to be 0.3 mg/L. Based on
  - RSD of 14% for Aqua America experiments conducted at known concentration of 0.2 mg/L
  - Assumption that standard deviation is known, results are normally distributed
- Systems will have to operate at a higher disinfectant residual to meet the standard and avoid public notifications
- Additional impacts of higher operating levels
  - Costs
  - DBP formation

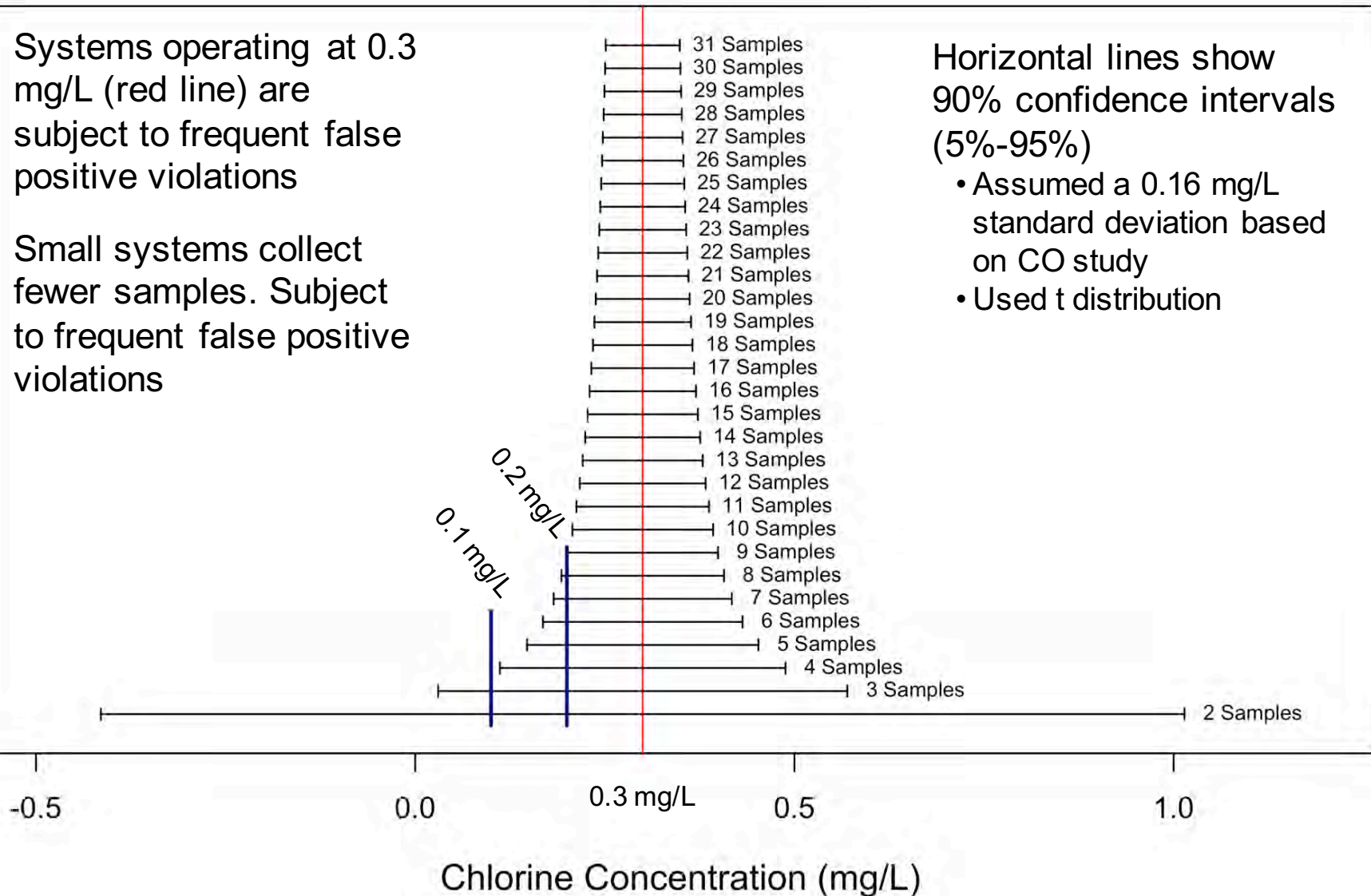
# False Positive Violations

Systems operating at 0.3 mg/L (red line) are subject to frequent false positive violations

Small systems collect fewer samples. Subject to frequent false positive violations

Horizontal lines show 90% confidence intervals (5%-95%)

- Assumed a 0.16 mg/L standard deviation based on CO study
- Used t distribution

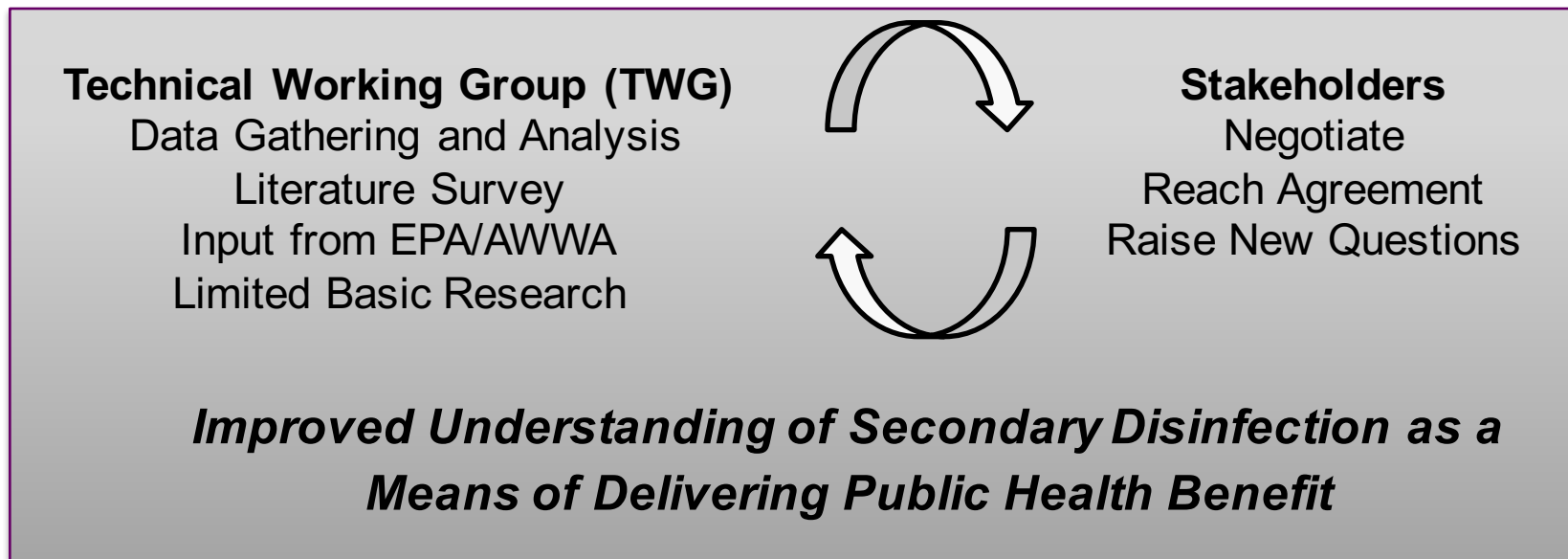


# Conclusions

- Studies indicate that a chlorine residual is detectable near 0.09 mg/L.
- We cannot measure disinfectant residual to an accuracy of hundredths of mg/L. Regulatory minimum residual levels should reflect this reality
- Variability and uncertainty in residual concentrations
  - necessitate distribution system operating levels significantly above a minimum residual level and
  - make misclassification (both false positives and false negatives) likely in small systems that collect few samples

# Toward a Better Regulations Development Process

- Obvious that secondary disinfection science is not yet sufficiently understood
- A FACA-like process would help this and other regulation development processes





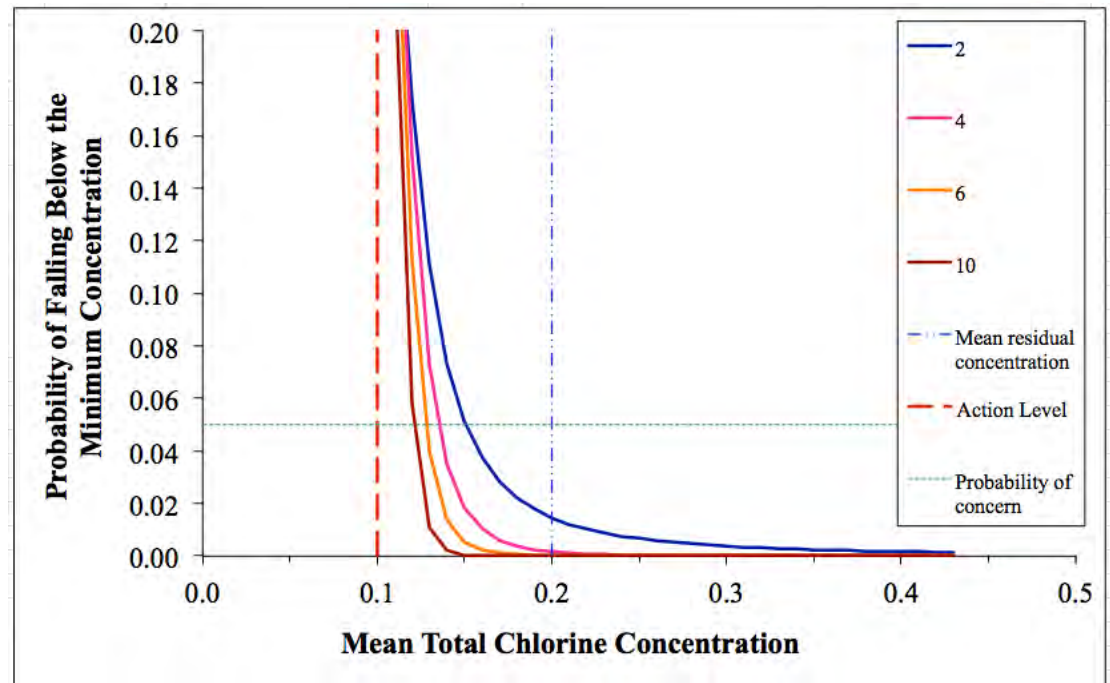
# Questions, Discussions, Acknowledgements

- Thanks to PW, PA AWWA and the PA drinking water community for their leadership on this topic
- Corona will continue to support this effort and others to develop policy for producing and delivering safe drinking water
- Jeff Rosen – [jrosen@coronaenv.com](mailto:jrosen@coronaenv.com)
- Questions?

# EXTRA SLIDES

# Uncertainty and Variability

- Estimates of uncertainty and variability in Colorado study are far in excess of the manufacturers declared variability
- Manufacturer's estimate of variability is different than real operational variability
- Tool to the right shows statistically where utilities will operate to meet the standard

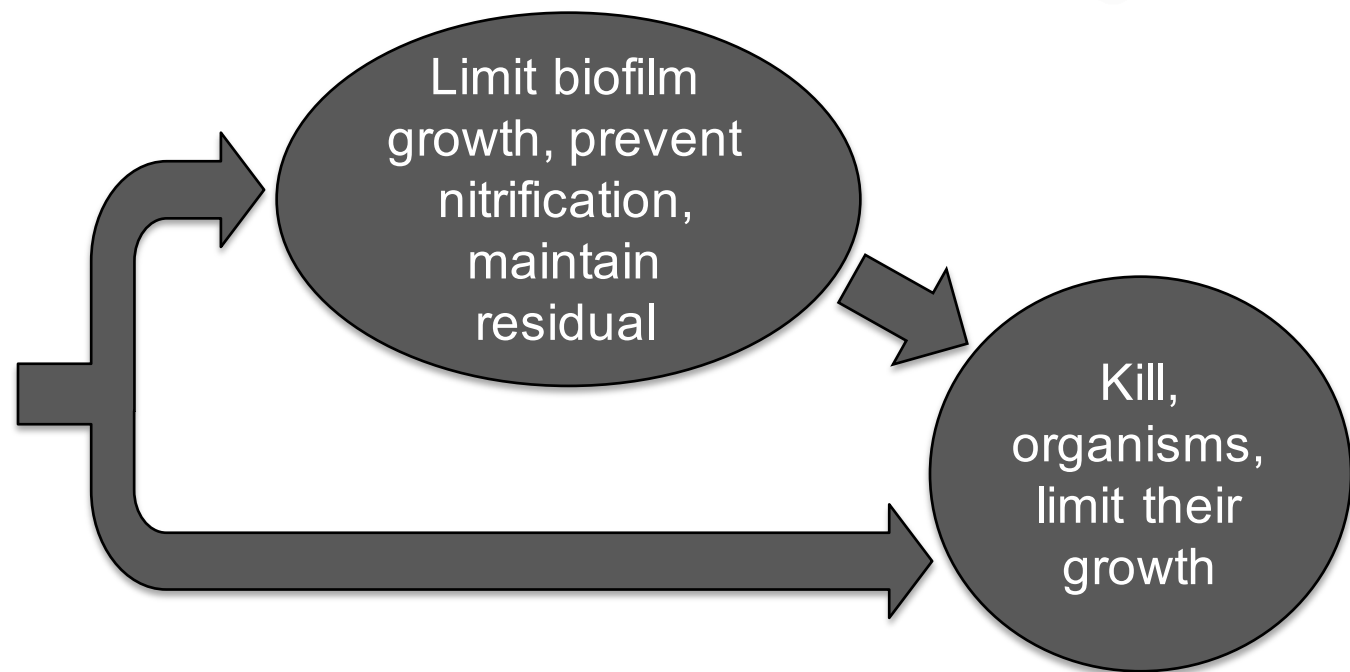


Enter the mean disinfectant residual concentration (mg/L)		0.2	User Input
Enter the Standard Deviation of the disinfectant residual concentration =====>		0.031	
Enter level of concern		0.1	
Sample Sizes to Evaluate	Lowest	2	
	2nd	4	
	3rd	6	
	Highest	10	
Enter the probability level of concern (usually 0.05) =====>		0.05	

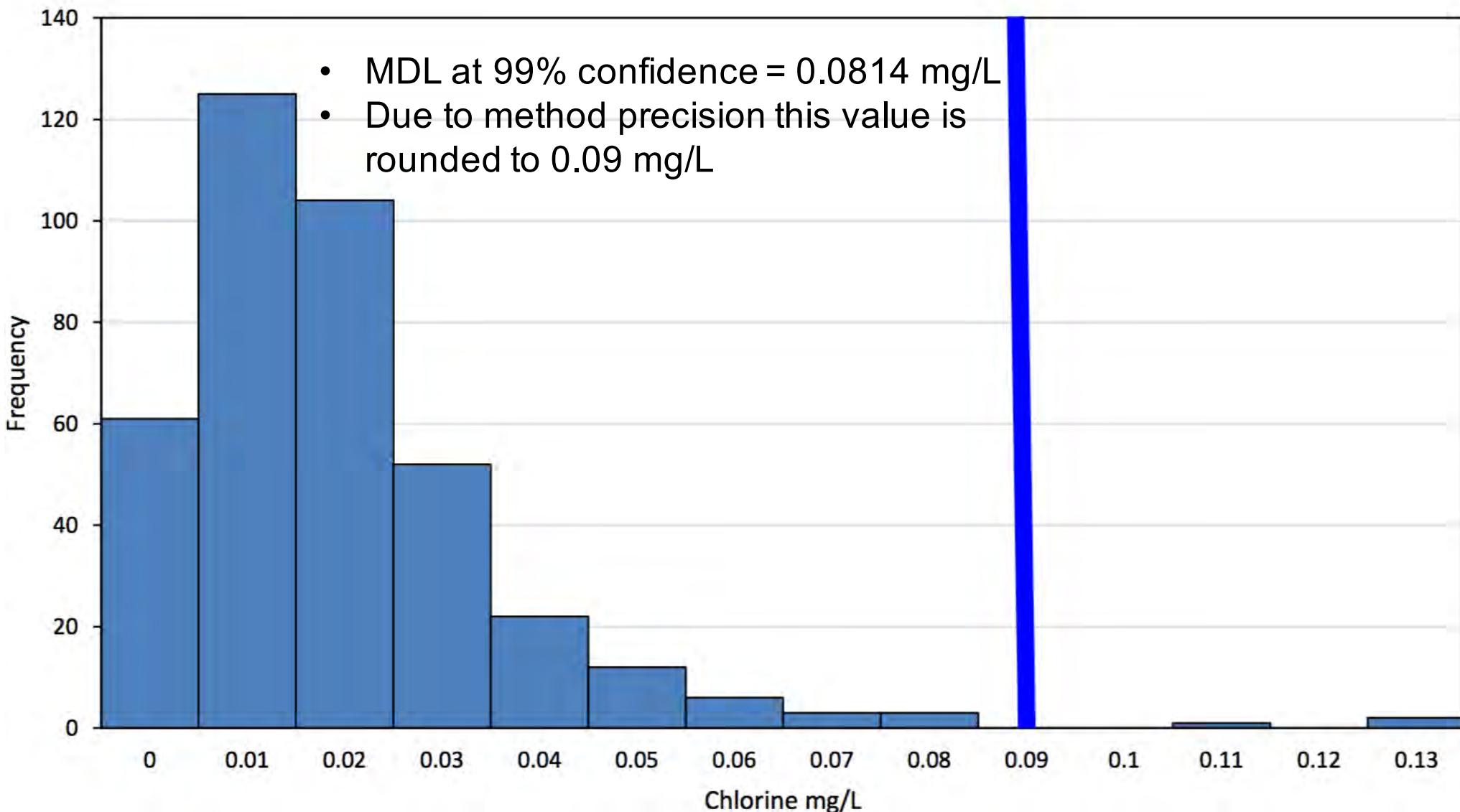
# Secondary Disinfection Overview

**Goal:** Prevent regrowth and human exposure to high doses of harmful microbes

**Roles:** (i) prevent conditions favoring growth  
(ii) kill/injure/limit organisms



# CO Study Statistical Analyses: PWS Samples with Dechlorinating Agent



# The Significance of Significant Digits

Type of Test	Working Range (mg/L)	Expected Precision (%)
Amperometric Titration	0.1-10	0-10
Colorimetric DPD Ferrous Titration	0.01-10	2-7
Colorimetric DPD	0.01-10	5-75

From Gordon et al. (1992). *Disinfectant Residual Measurement Methods*. Second Ed, AWWARF and AWWA

# The Significance of Significant Digits

- Even the most sensitive methods used under the most controlled conditions cannot detect differences of 0.01 mg/L
- Rounding:
  - ❑ 0.15 mg/L rounds up to 0.2
  - ❑ 0.14 mg/L rounds down to 0.1 mg/L