Application of Detection and Quantification Concepts to Chlorine Residual Measurements

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PADEP Proposed Disinfection Requirements Rule
Stakeholder Meeting
Harrisburg, PA

March 9, 2016

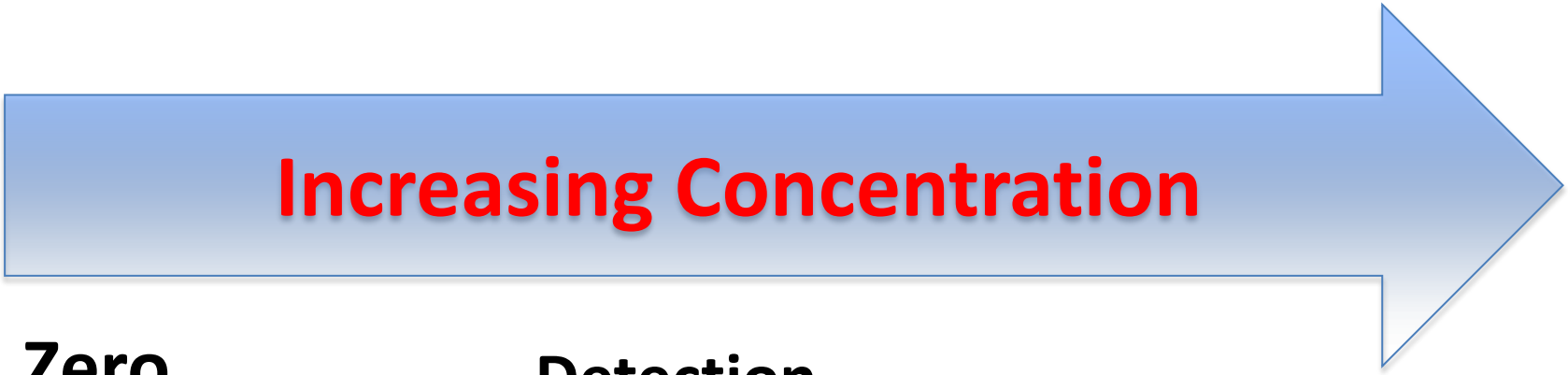
Outline

- Quantification (Reporting Level) concept is at heart of PADEP's proposed regulation

- Overview of detection and quantification
  - Focus on MDL and MRL
  - Example calculations

- Key Points
  - Detection and quantification are two different concepts
  - Laboratory activities may not be familiar outside of labs
  - Long history of confusion with concepts

Detection is <u>not</u> the same as quantification



Zero

Detection

MDL
LOD
DL
RDL

Quantification

MRL
LOQ
RL
ML
PQL
RQL
LCMRL

J value

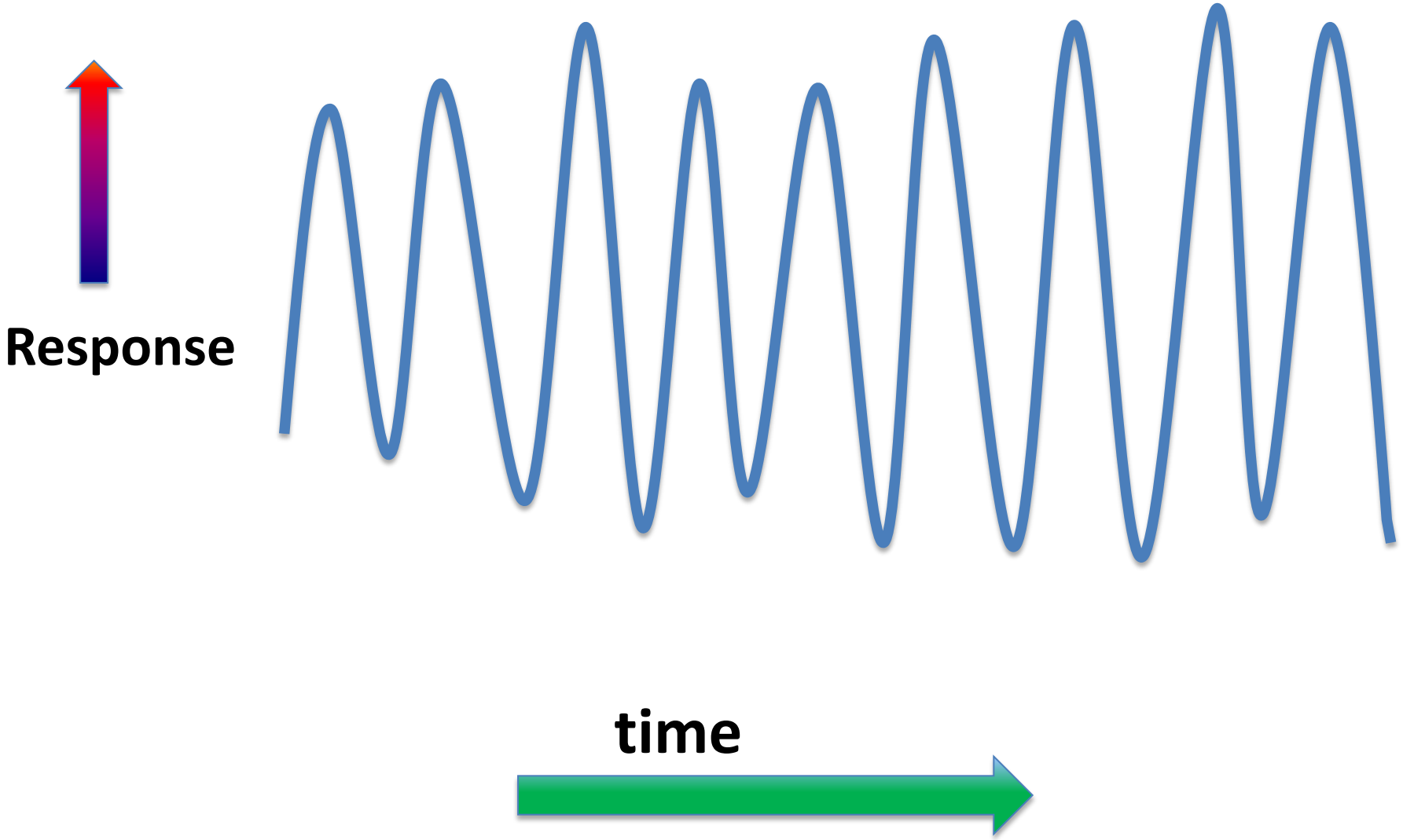
Detection and Quantification

Two general approaches

- **Blank response** (baseline): classical approach
- **Analyte response**: EPA's Method Detection Limit

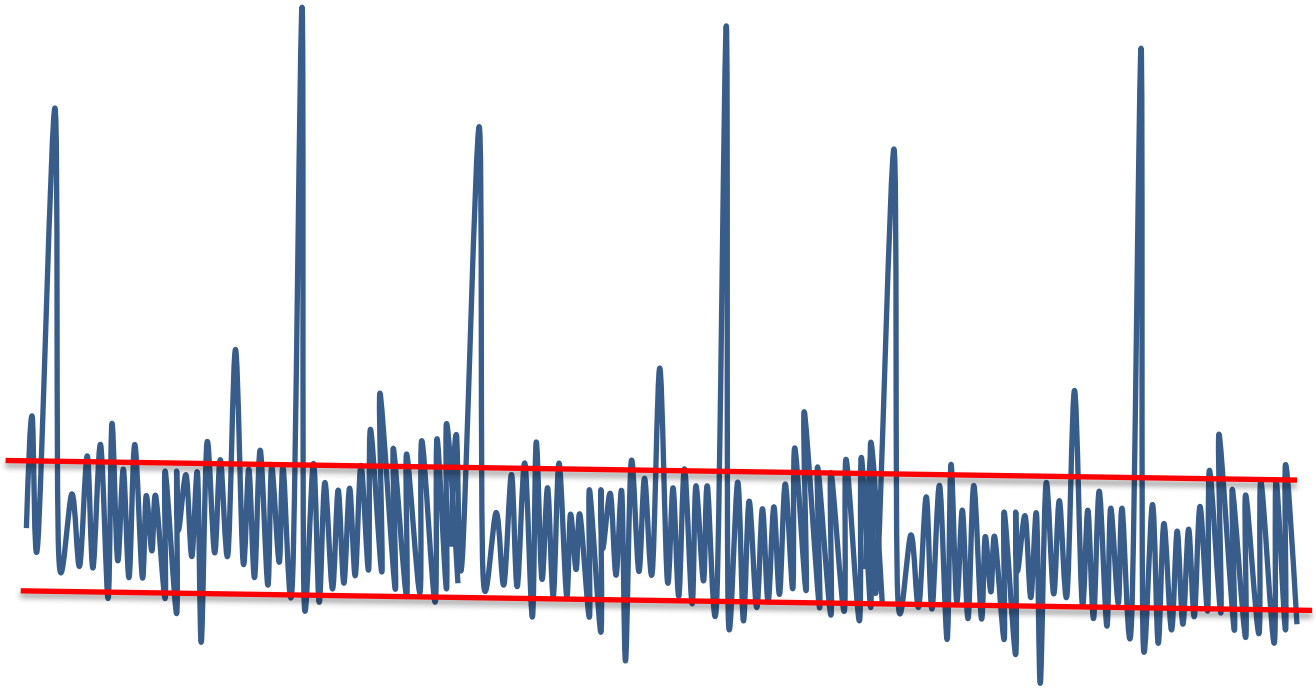
Variation of blank (no added analyte)

Instrument Response Over Time



Challenge of Measurement Process:

Distinguishing baseline response from a quantifiable analyte result



Instrument Response Over Time

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Detection Concept

- Detection
- Limit of Detection
- Method Detection Limit (MDL)
- Method Detection Level
- Lower Limit of Detection
- Critical value
- Reliable Detection Level
- **No universally accepted definition**

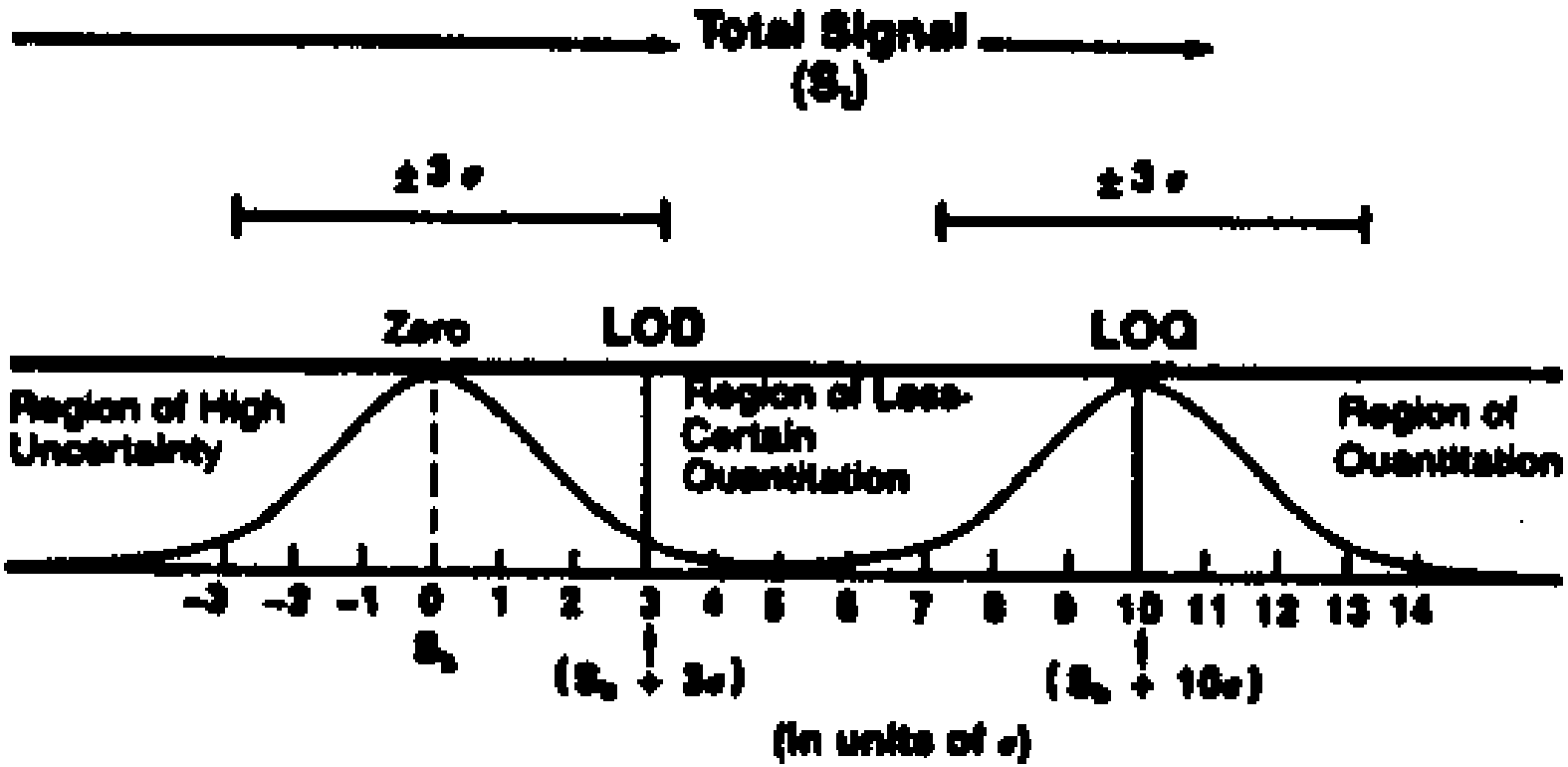

Figure 4. Relationship of LOD and LOQ to signal strength. The LOD is located 3σ above the measured average difference in the total (S_t) and blank (S_b) signals; the LOQ is 10σ above S_b.

Analytical Chemistry, *55(14):2210–2218.*

Method Detection Limit

What is an MDL and how is it calculated?

- Defined in Federal Register, 40 CFR 136
- Specific definition
  - Derived from Glaser et al, 1981, ES&T paper
  - Calculation required in many analytical methods published by EPA

APPENDIX B TO PART 136—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT—REVISION 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, *i.e.*, a break in the slope of the standard curve.

the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$$MDL = T_{(n-1,1-\alpha=0.99)} \quad (S)$$

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha=.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$\left[6S_A^2 + 6S_B^2\right]^{\frac{1}{2}}$$

Method Detection Limit

simple and specific calculation

$$MDL = t * SD$$

t value is a *constant* for a given number of analyses
typically 3.143 for 7 replicates

SD = Standard Deviation

MDL is a measure of ***precision***

Method Detection Limit

What is an MDL and how is it calculated?

<u>In the laboratory</u>

- Precision of replicate measurements (typically 7)
  - Replicates in succession
  - Replicates on different days
- Analysis of known concentrations in reagent water
- Spike concentration is selected by analyst
- Criteria to determine if MDL "*worked*"
- Does not account for interferences or matrix effects

MDL Calculation: bogus data

Spike Concentration Value = 0.1 ug/L		
Analyst	**Replicate**	**Concentration Determined, ug/L**
fake	1	0.1
fake	2	0.1
fake	3	0.1
fake	4	0.1
fake	5	0.1
fake	6	0.1
fake	7	0.1
	Average	0.100
	Average % Recovery	100 %
	Standard Deviation	0.000
	% RSD	0 %
	MDL	0.000

Calculated MDL can be unrealistically low

MDL Calculations: bogus data

Analyst	Replicate	Concentration Determined, ug/L	Concentration Determined, ug/L	Concentration Determined, ug/L
fake	1	0.05	0.15	0.45
fake	2	0.05	0.15	0.45
fake	3	0.1	0.2	0.5
fake	4	0.1	0.2	0.5
fake	5	0.1	0.2	0.5
fake	6	0.14	0.24	0.54
fake	7	0.14	0.24	0.54
	Average	0.097	0.197	0.497
	Average % Recovery	97 %	99 %	99 %
	Standard Deviation	0.037	0.037	0.037
	% RSD	38 %	19 %	7 %
	MDL	0.116	0.116	0.116

Chlorine Residual by DPD Method

Spike Concentration = 0.1 mg/L **6/11/2015**

Analyst	Replicate	Total Chlorine, mg/L
RJC	1	0.11
RJC	2	0.11
RJC	3	0.11
RJC	4	0.11
RJC	5	0.11
RJC	6	0.12
RJC	7	0.15
RJC	8	0.11

Average	0.116
Average % Recovery	116 %
Standard Deviation	0.014
% RSD	12 %
MDL	**0.042**

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Chlorine Residual by DPD Method
Spike Concentration = 0.1 mg/L **6/15/2015**

Analyst	Replicate	Total Chlorine, mg/L
TSG	1	0.12
TSG	2	0.12
TSG	3	0.13
TSG	4	0.13
TSG	5	0.12
TSG	6	0.13
TSG	7	0.12
TSG	8	0.12
TSG	9	0.13

Average	0.124
Average % Recovery	124 %
Standard Deviation	0.005
% RSD	4 %
MDL	**0.015**

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Chlorine Residual by DPD Method
Spike Concentration = 0.1 mg/L

6/16/2015

Analyst	Replicate	Total Chlorine, mg/L
KHD	1	0.11
KHD	2	0.11
KHD	3	0.15
KHD	4	0.12
KHD	5	0.11
KHD	6	0.13
KHD	7	0.12
KHD	8	0.12

Average	0.121
Average % Recovery	121 %
Standard Deviation	0.014
% RSD	11 %
MDL	0.041

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Quantification Concept

- Limit of Quantification
- Limit of Quantitation
- Practical Quantitation Limit (PQL)
- Practical Quantitation Level
- Reliable Quantitation Level
- Minimum Level
- Minimum Reporting Limit
- Minimum Reporting Level (MRL)
- Reporting Level
- Reporting Limit
- Lowest Concentration MRL
- **No universally accepted definition**
  - **Multiple of detection level**
  - **Independent derivation**

Minimum Reporting Level

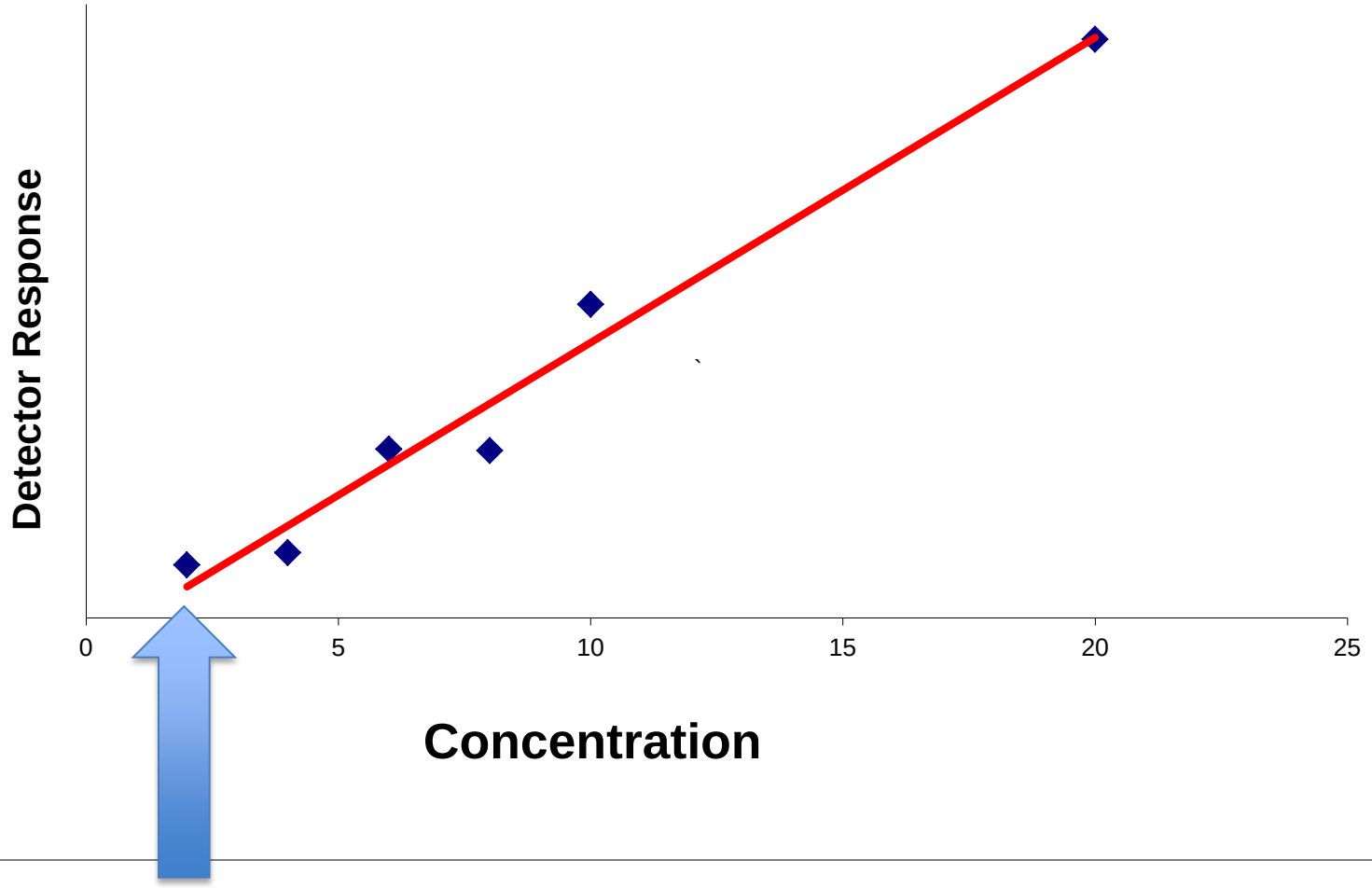
- No universal procedure
- EPA has used MRL concept in analytical methods since 1990s
- EPA used concept in Unregulated Contaminant Monitoring Rules…starting with UCMR1
- Policy in Aqua PA laboratory
  - MRL is lowest point in calibration curve

Minimum Reporting Level

- Set to the convenience of the laboratory
- Two goals of accredited labs
  - Meet the needs of clients
    - ensure that drinking water standards are achieved*
  - Maintain accreditation
    - pass PT samples
    - meet QC within method
- Goals do not always align
  - Example: nitrite

**Ideal situation*: analytical method is very sensitive; high ratio of MCL : PQL

Calibration Curve



Minimum Reporting Level

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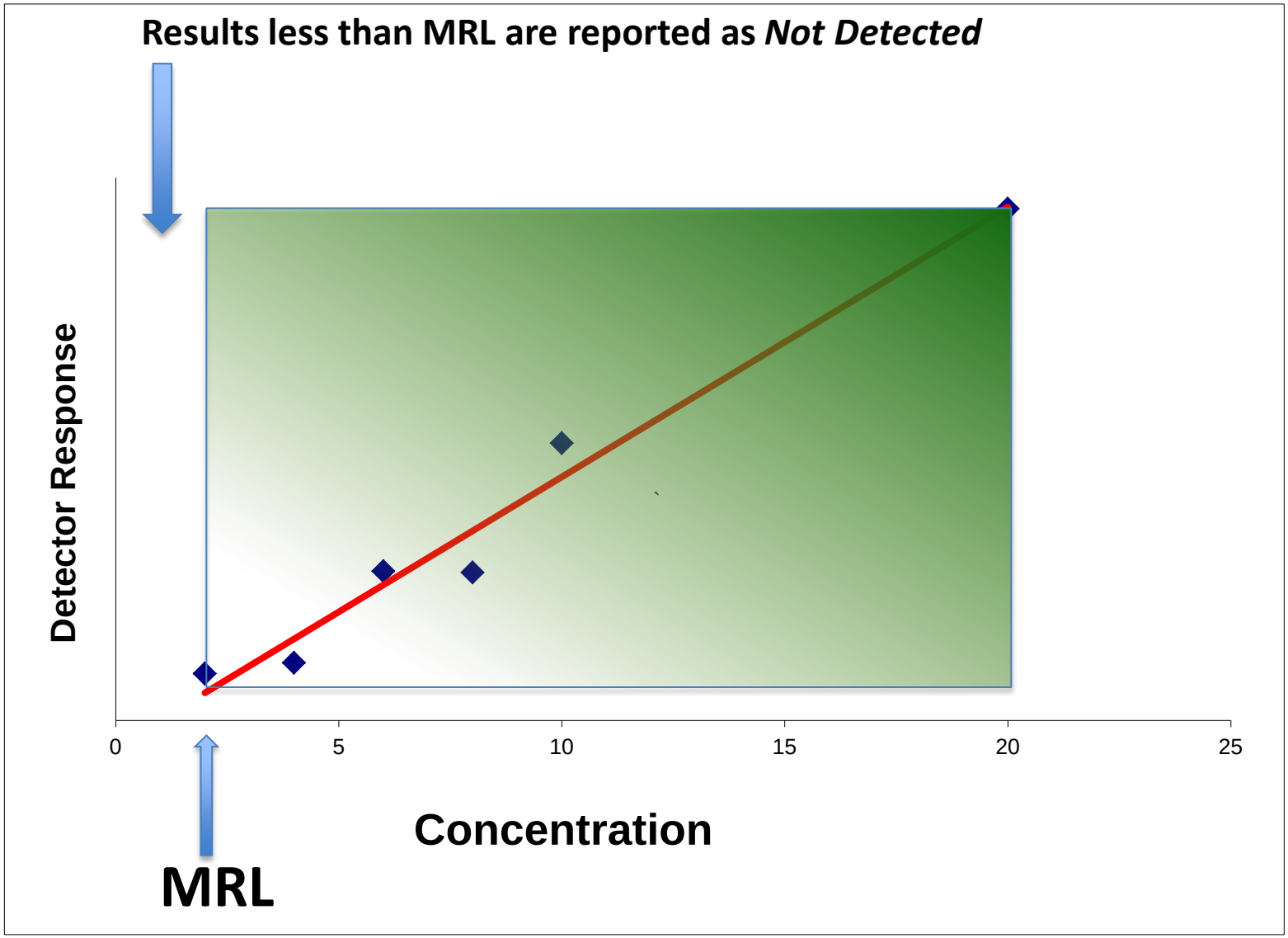
Results are reported only when they are in range of calibration curve



Minimum Reporting Level

- Low end of calibration curve
- Results < MRL → Not Detected
- Still does not account for matrix effects or interferences
- Quantification level, such as MRL, is key to setting minimum disinfectant level

Key Points: detection and quantification

- Concepts are important in environmental analyses
  especially with low level analyses
- Key features of analytical methods
- Terminology is confusing
- Attempts to minimize confusion over the years
- MDL is one (important) detection concept
  - Calculation is required in many methods
  - Calculation is straightforward
  - Interpretation can be misleading
- Quantification is what really matters

Key Points

- Aqua strongly supports an on-going technical discussion about increasing the minimum disinfectant residual.
- Setting a minimum disinfectant residual in the distribution system has major impacts, including potential unintended consequences
- Disinfectant residual is just one component in a complex and multi-faceted approach to public health protection.
- Quantification level, such as MRL, is key to setting minimum disinfectant residual

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March 9, 2016