FDEP and SFWMD Data Comparability

Frank Nearhoof
FDEP

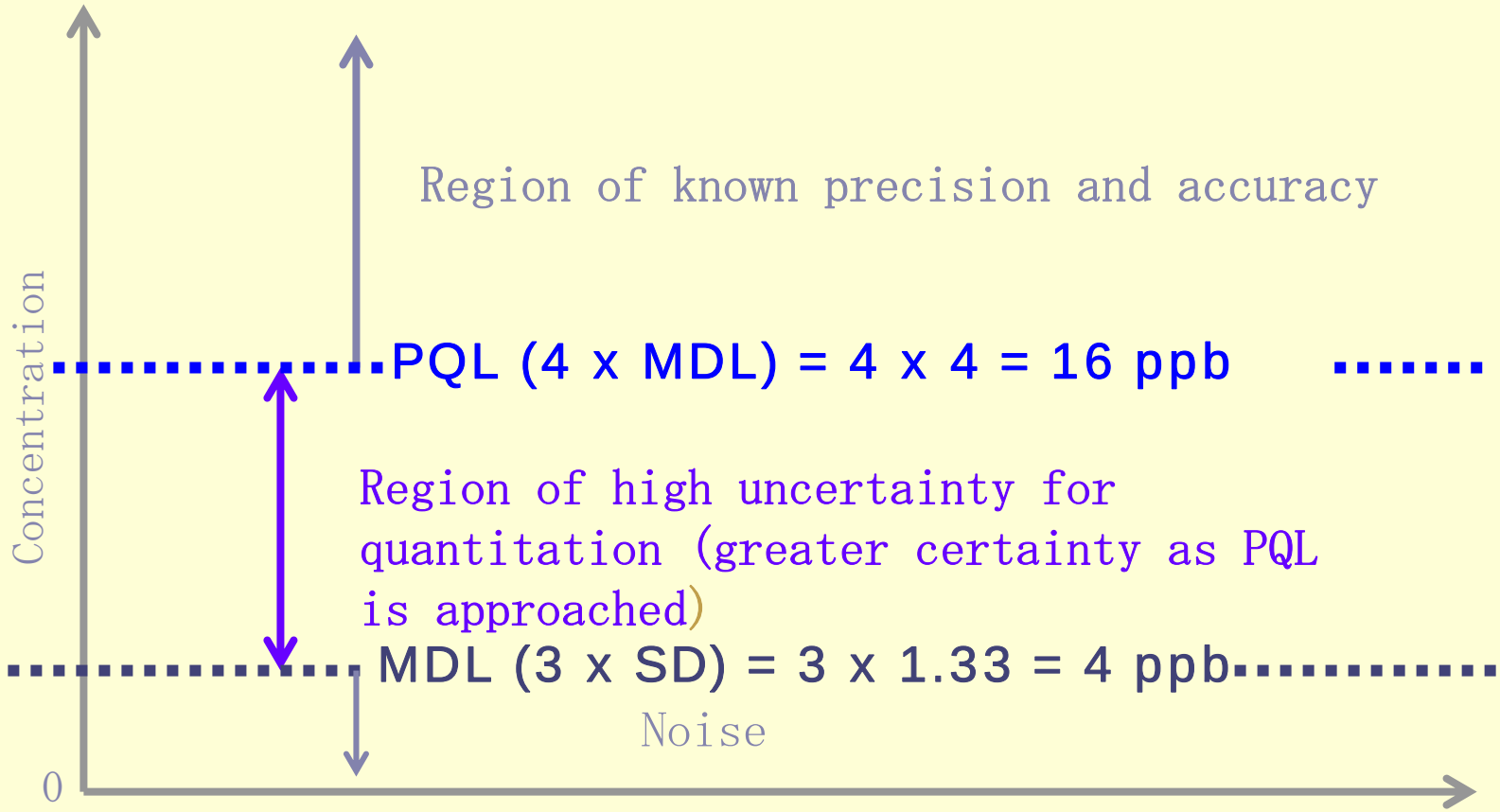
2003 QA Report

Table 6. Results of TP split study between SFWMD and FDEP laboratories, EVPA Project, 15-Dec-03

Station	Date Collected	Sample Type	TPO4 Results (mg/L)		Difference (SFWMD-FDEP)	% RPD	Comments
			SFWMD	FDEP			
S5AD	15-Dec-03	EB	<0.002	<0.004	<MDL	N/A	<PQL
S5AD	15-Dec-03	SS	0.127	0.150	-0.023	16.6	Acceptable< 20% RPD
LOX3	15-Dec-03	SS	0.010	0.015	-0.005	40.0	Very heavy suspended solids
LOX5	15-Dec-03	SS	0.011	0.013	-0.002	16.7	<PQL
LOX10	15-Dec-03	SS	0.013	0.018	-0.005	32.3	Very heavy suspended solids

Detection and Quantitation Limit Concepts

MDL/PQL Relationship



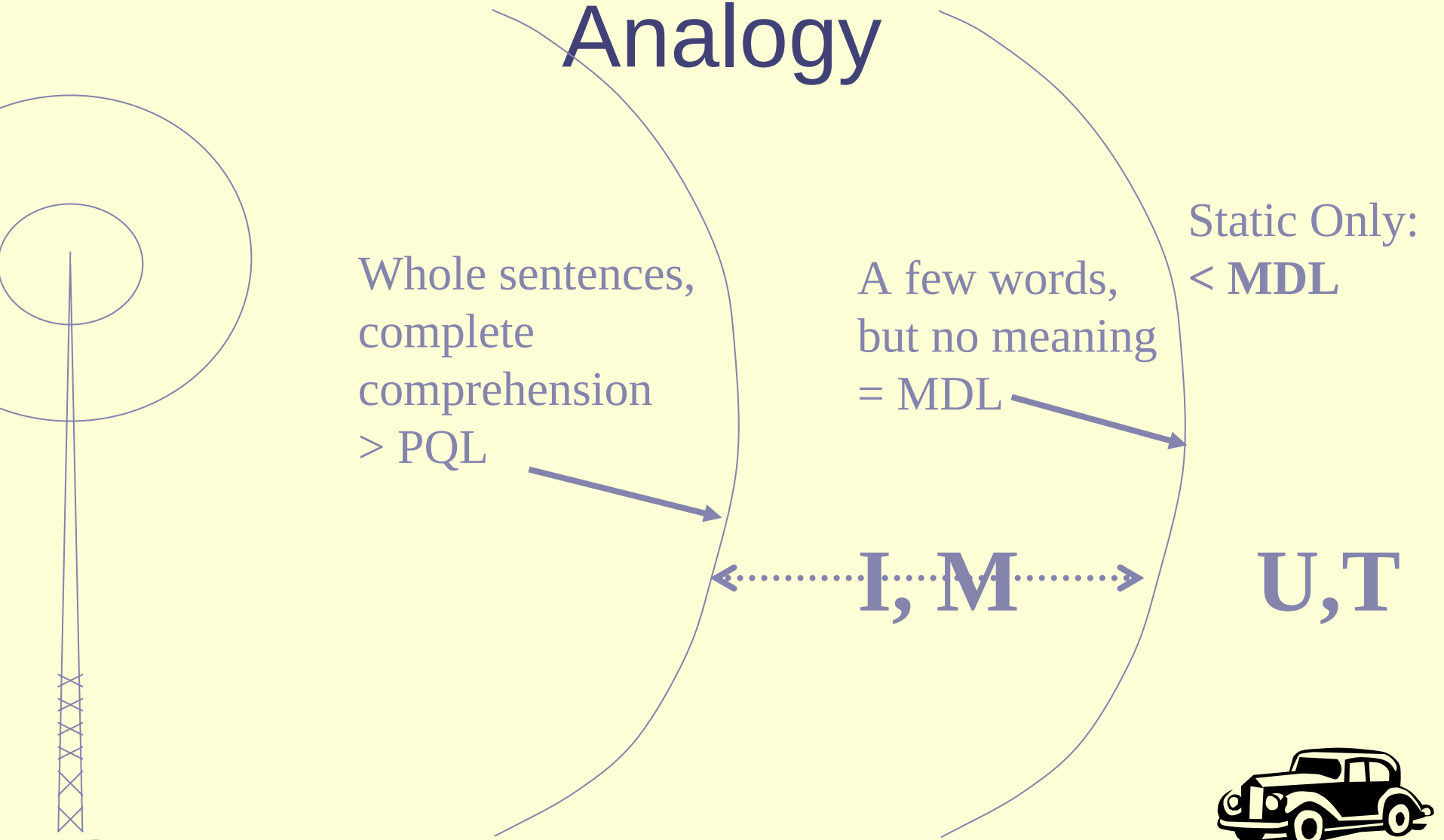
Definitions

- **Minimum Detection Limit (MDL)**: The minimum concentration that can be measured with 99% confidence that the analyte concentration is greater than zero.
  - FDEP = 4 ppb
  - SFWMD = 4 ppb (<9/17/02); 2 ppb (>9/17/02)

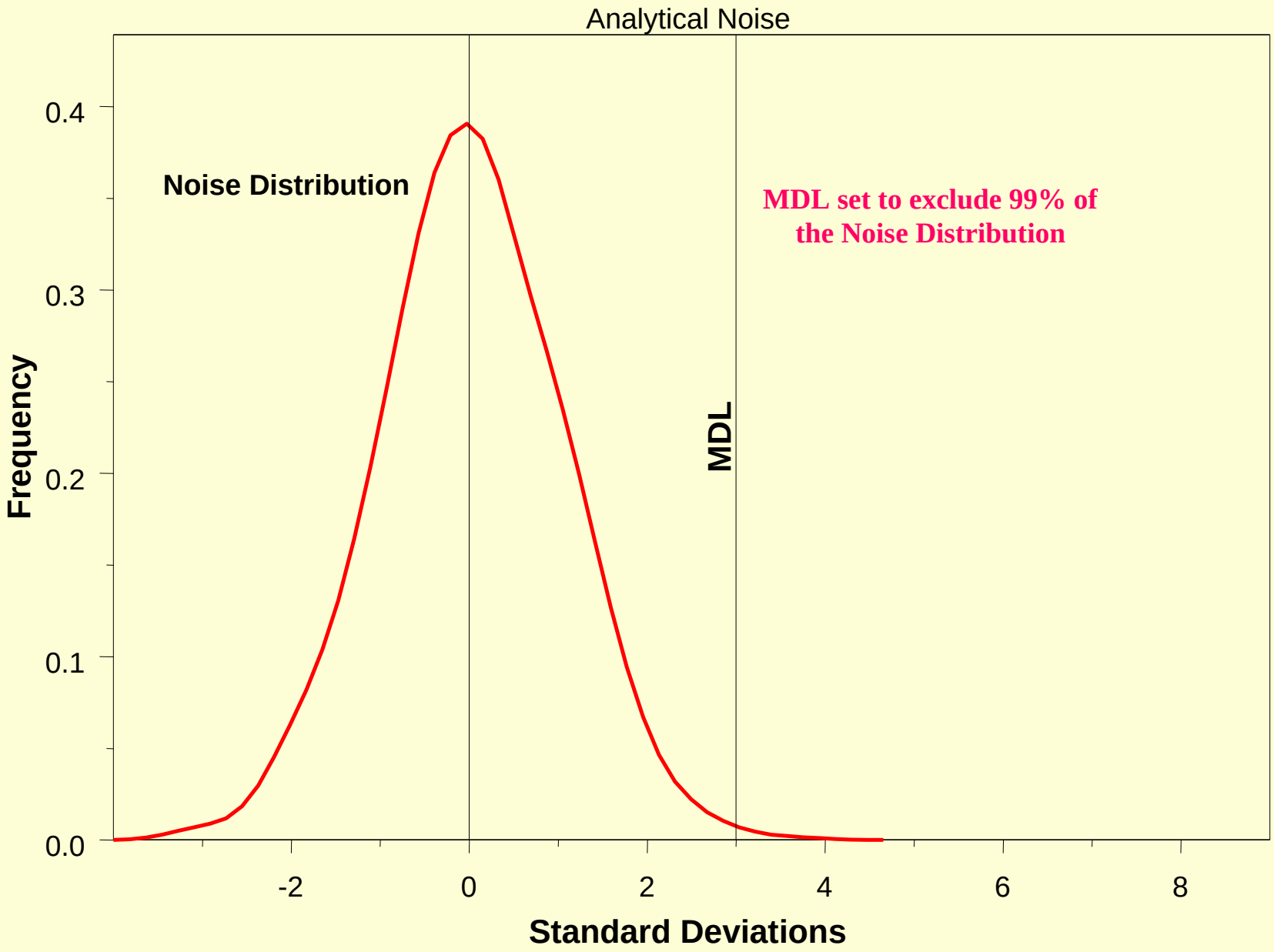
Definitions

- **Practical Quantitation Limit (PQL)**: The lowest level of measurement that can be reliably achieved during routine laboratory operating conditions within specified limits of precision and accuracy.
- **Two methods to derive:**
  - Calculated (FDEP) = 10 ppb
  - Default (SFWMD) = 4 x MDL = 16 ppb (<9/17/02); 8 ppb (>9/17/02)

MDL/PQL Radio Reception Analogy



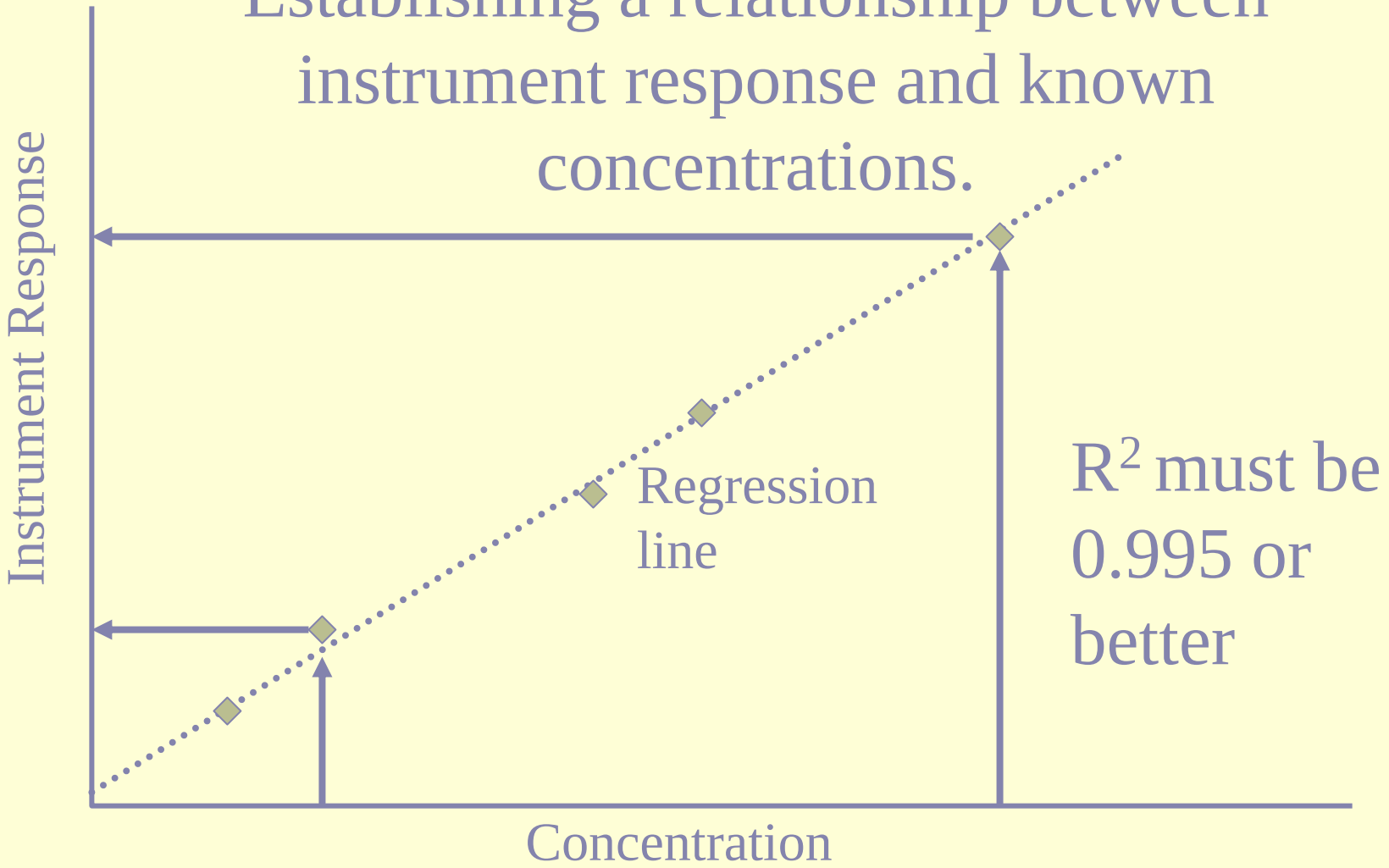
Theoretical Probability Distributions



Examples of Required Laboratory QC Activities

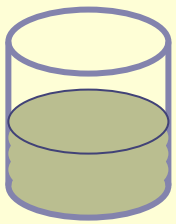
Calibration

Establishing a relationship between instrument response and known concentrations.



Performance Test Samples

- NELAC required “Blind” sample, lab does not know concentration of analyte.
- Lab runs PT sample using routine procedures.
- Must achieve acceptable result in 2 PTs per year.



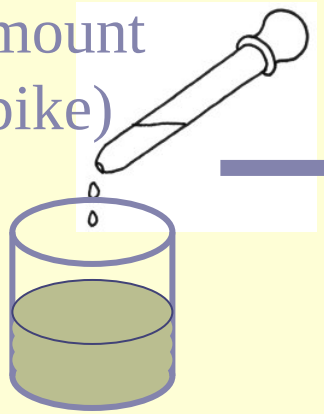
Unknown

Result must be within range

Lab Control Sample (LCS)

- A known concentration of analyte added
- Sample processed routinely.
- Determine if amount detected matches amount added (+ or – acceptable %).

Add known Amount (spike)



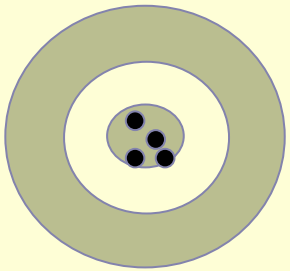
Determine % recovery

Acceptance criteria is usually 80% to 120%

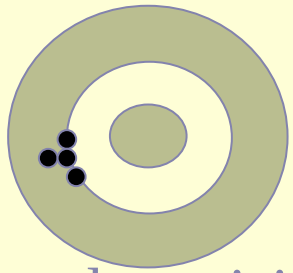
Precision and Accuracy

- Accuracy: The ability to measure the “true” value.
  - True value is NIST standard
- Precision: Consistency of measurements.

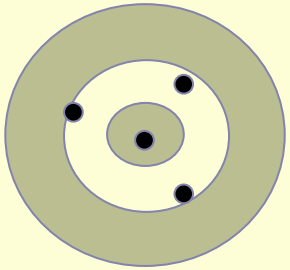
Why Quality Control Samples are Important



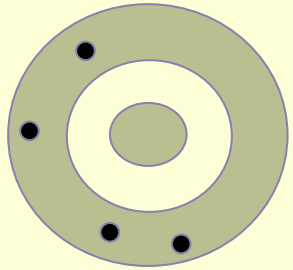
Good precision,
Good accuracy



Good precision,
Poor accuracy



Poor precision,
Good accuracy



Poor precision,
Poor accuracy

Laboratories Have Collaborated for Over a Decade to Ensure and Enhance Data Comparability

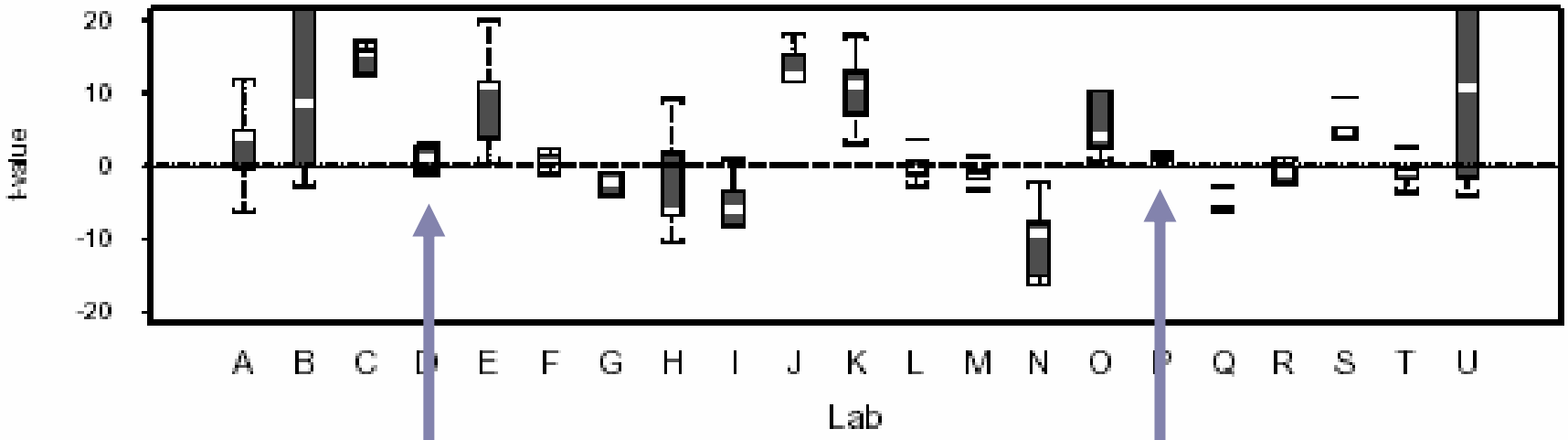
- Everglades Round Robin
  - Initiated in 1995
  - Conducted to determine relative agreement of laboratories
  - Blind samples sent to participating labs (20+ labs)
    - Initially twice per year
    - Now once per year
  - Included FDEP, SFWMD, university and commercial labs
  - 14 iterations through October 2003
  - 13 statistical reports
  - Next iteration scheduled for 2004

Laboratories Have Collaborated for Over a Decade to Ensure and Enhance Data Comparability

- Routine chemists meetings
- Additional split studies implemented as part of SFWMD studies
- Continuous communication between SFWMD & FDEP lab staff
- SFWMD and FDEP troubleshooting of lab and field studies

Example of RR Results (ERR #6 : Summary of 5 Samples)

Line indicates central tendency of all measurements



FDEP
(Scored 4.6)

SFWMD
(Scored 5.0)

0=unacceptable; 5=excellent

Summary of RR Scores
(based on t-value and C-W distance)

N=13	FDEP	SFWMD
Mean Score	4.3	4.3
Std. Dev	0.5	0.7

Identical scores!!

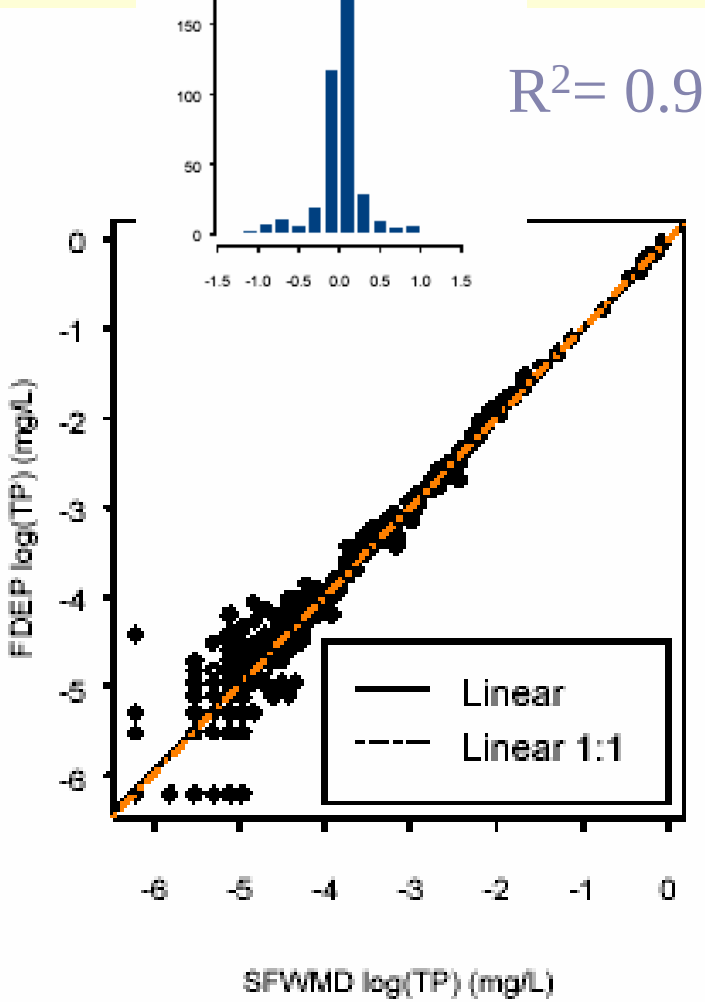
Both labs in the “good” to “very good” range.

Consistently among the best performing labs.

Comparing FDEP to SFWMD TP Measurements

- 423 split and duplicate samples since 2002
- Regression analyses is best statistical tool for this comparison
  - Logarithm transformation needed when data distribution is skewed
  - Transformation not needed in range (<20 ppb) where distribution is approximately normal
- 95% Confidence Intervals should be applied to linear relationship

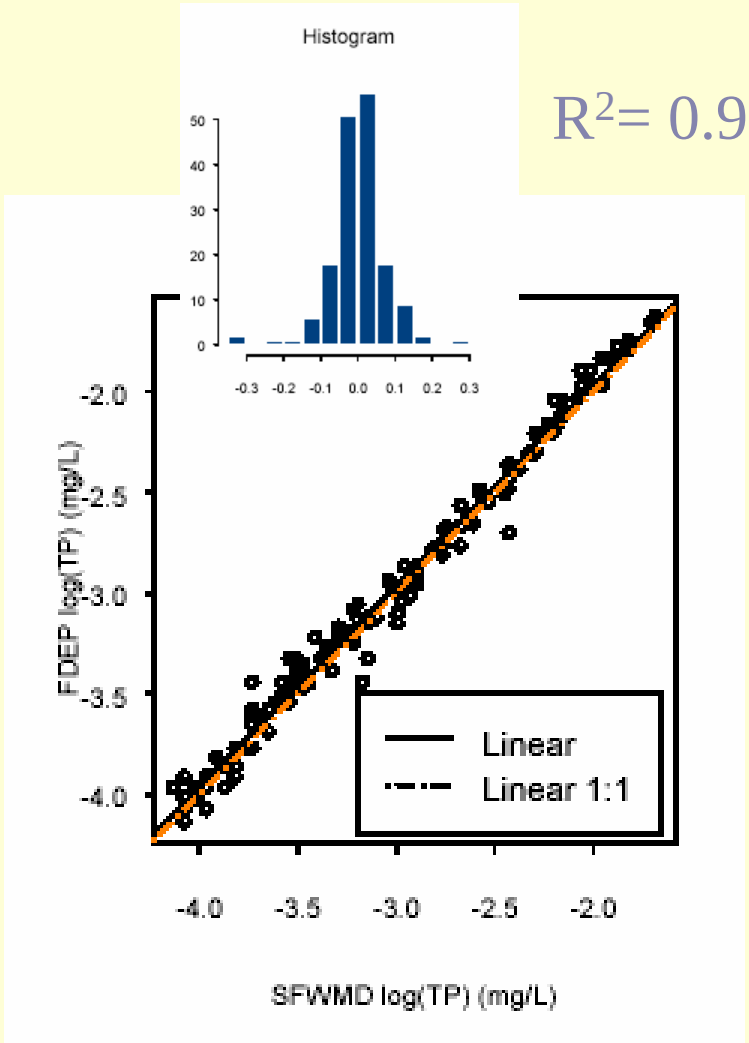
Regression: FDEP vs. SFWMD, All data



Conclusions:

- **The intercept is not different from 0 statistically since the 95% CI for intercept contains 0.**
- **The slope is not different from 1 statistically since the 95% CI for slope contains 1.**
- **Overall, the labs correlate very well.**

Regression: FDEP vs. SFWMD, 16 ppb to 200 ppb range



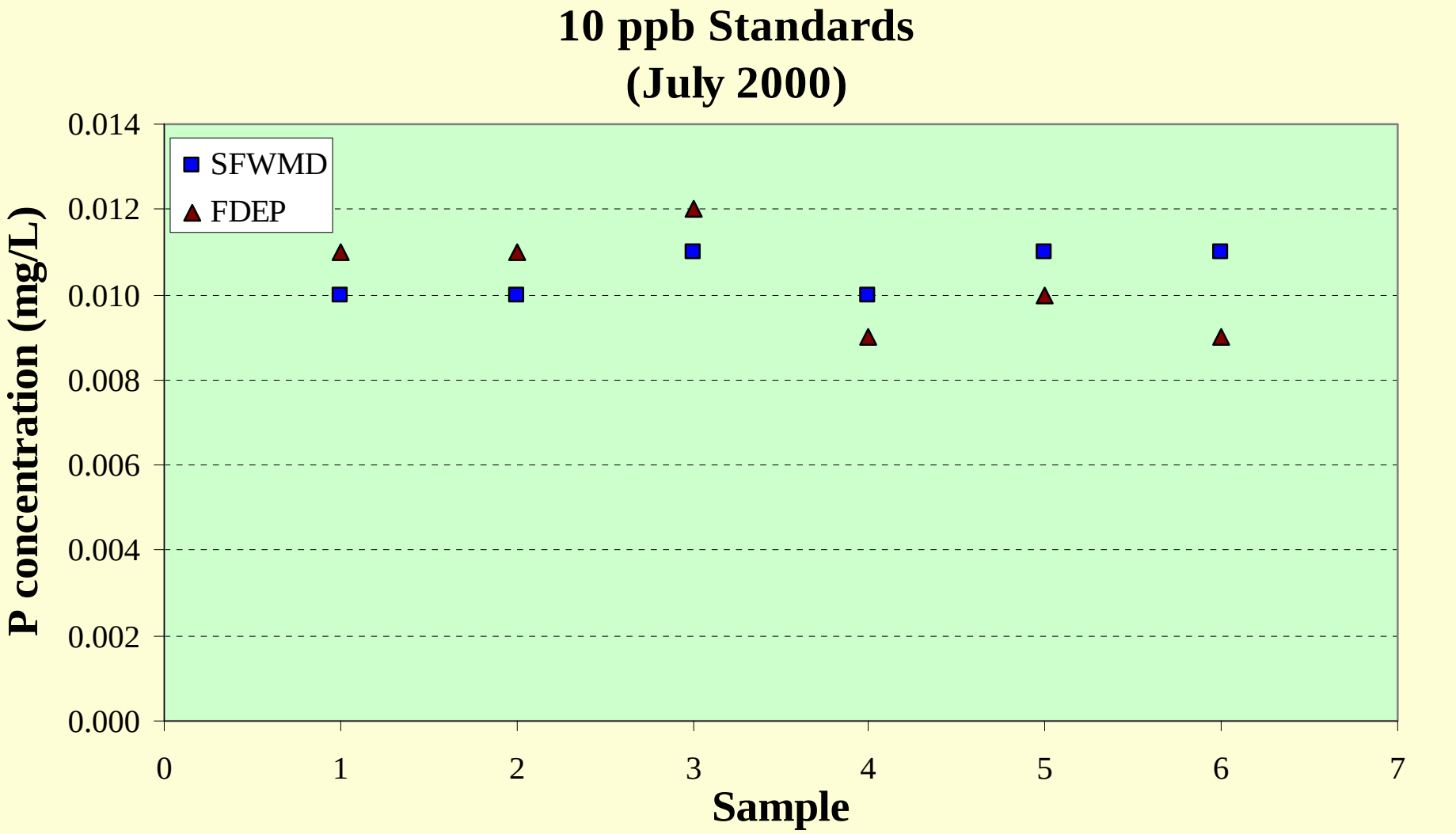
$R^2 = 0.98$

Conclusions:

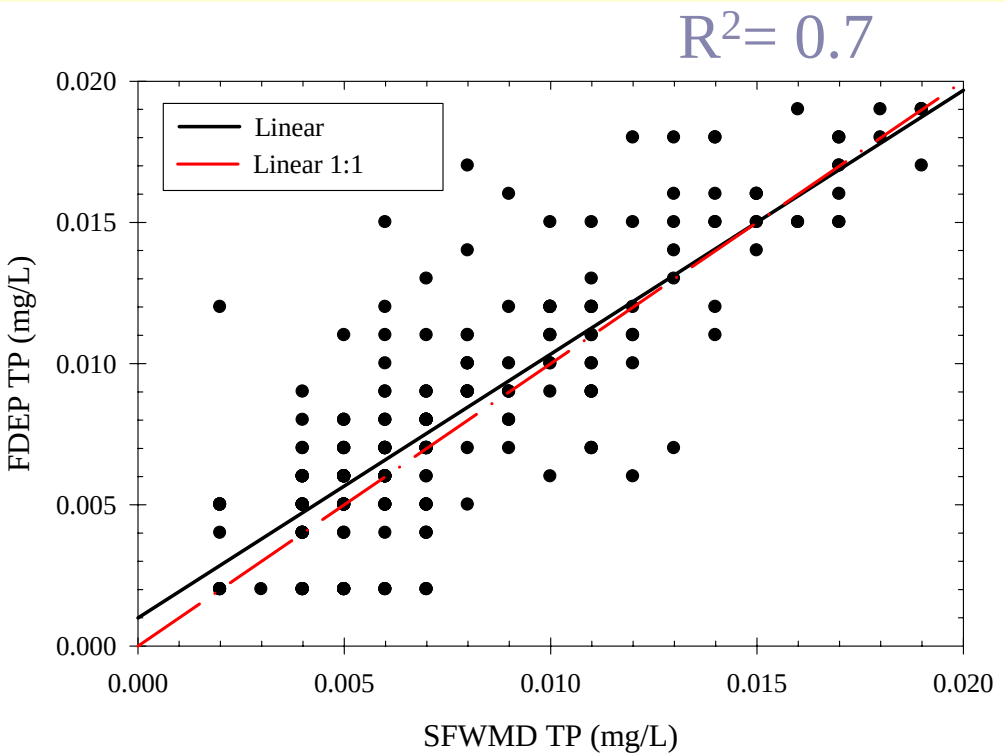
- **The intercept is not different from 0 statistically since the 95% CI for intercept contains 0.**
- **The slope is not different from 1 statistically since the 95% CI for slope contains 1.**

FDEP vs SFWMD < 20 ppb

- 254 split and duplicate samples - June 2000 – March 2004
- Programs:
  - 10 ppb standards
  - ERR
  - C-111
  - EVPA (Lox)


10 ppb Standards
(July 2000)
P concentration (mg/L)
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
SFWMD
FDEP
0
1
2
3
4
5
6
7
Sample

Regression: FDEP vs. SFWMD, <20 ug/L

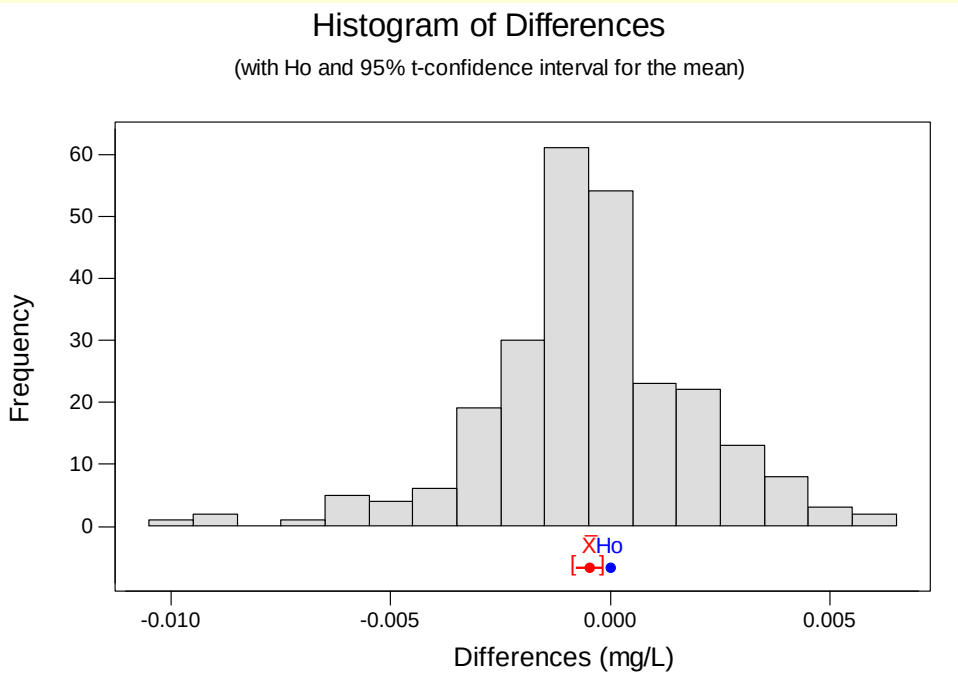


Conclusions:

- **Slope not statistically different from 1.**
- **Intercept is statistically different from 0, due to MDL considerations.**

Paired Tests: FDEP vs. SFWMD <20 ppb

	N	Median	Mean	95% C.I. Mean
SFWMD (mg/L)	254	0.007	0.0078	0.0073 to 0.0083
FDEP (mg/L)	254	0.007	0.0082	0.0077 to 0.0088
Paired Sample Difference (mg/L)	254	-0.001	-0.00048	-0.0008 to -0.0002



Paired t-test p= 0.002

Wilcoxon Signed Rank Test p=0.005

Conclusions:

- Small difference (**<1 ppb**) between labs based on paired tests
- Statistical power increases with sample size; i.e., can detect minor and inconsequential differences
- Both labs yield the same long-term average concentration

Conclusions

- Both labs yield same long-term average concentration.
- Both laboratories score consistently well in ERRs, average scores identical (4.3) in the good to very good range.
- Regression analyses indicate extremely good agreement between labs overall.
- Even in the low range (<20 ppb), absolute differences in measurements with very sensitive tests are very small.
  - MDL/PQL considerations