

# NYC Phosphorus Comparability Study

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# Acknowledgements

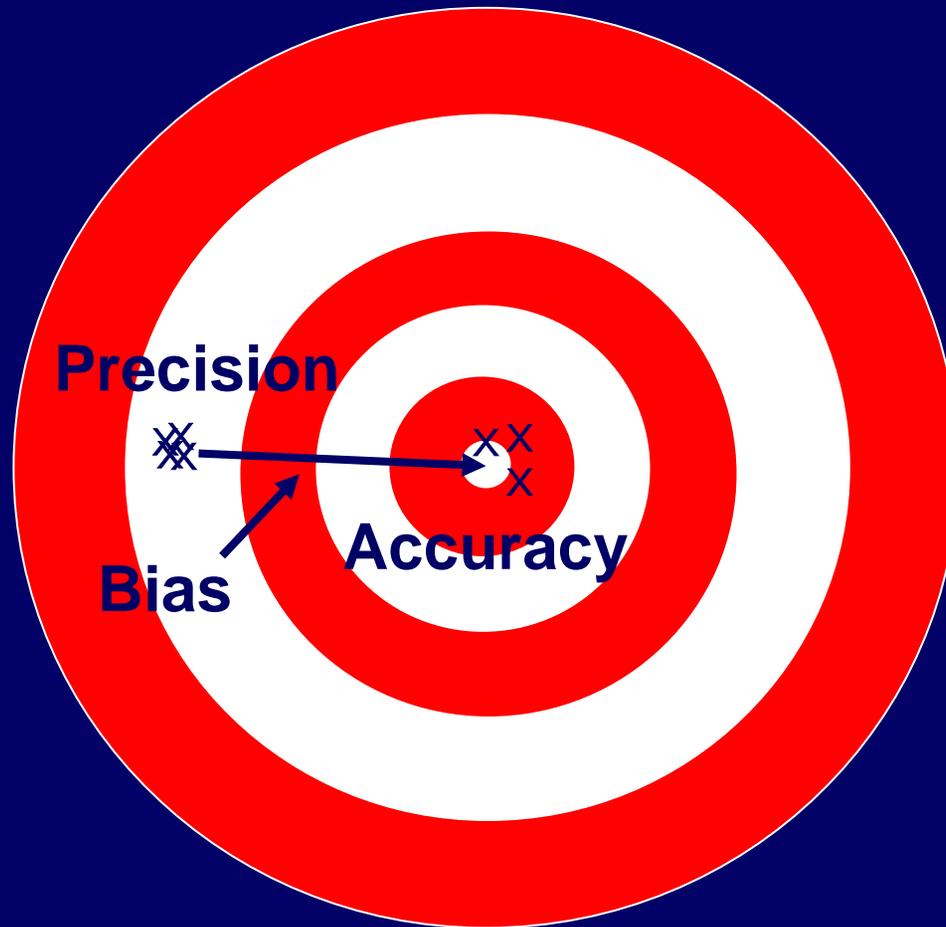
- 💧 **Merle Shockey** USGS - NWQL
- 💧 **Charlie Patton** USGS – NWQL
- 💧 **Harold Ardourel** USGS – NWQL
- 💧 **Tom Maloney** USGS – NWQL
- 💧 **Terry Schertz** USGS – BQS
- 💧 **Mark Woodworth** USGS – BQS
- 💧 **Mary Cast** USGS – BQS
- 💧 **Methods Board Nutrient Workgroup**
- 💧 **Participating Laboratories**

# Participating Laboratories

- 💧 **USGS – NWQL**
- 💧 **Columbia Analytical Services**
- 💧 **Upstate Freshwater Institute**
- 💧 **NYS - Department of Health**
- 💧 **University of Puerto Rico**
- 💧 **New York City Department of  
Environmental Protection**
- 💧 **Severn Trent Laboratories**
- 💧 **USDA – ARS (Penn State University)**
- 💧 **Philadelphia Academy of Natural Sciences**
- 💧 **Cornell University**

# On Target, but...

## What are we trying to measure?



# Why Bother?

- 💧 **Project designed to evaluate comparability between laboratories analyzing water for phosphorus**
- 💧 **Labs (except UPR) analyze P for samples collected in Catskill-Delaware NYC Reservoir Watershed.**
- 💧 **If data are to derive holistic determinations of water quality, sources, loadings, responses to change, etc., data comparability must be known**

# Sampling Methods

## Round 1

- ◆ 3 USGS SRS samples shipped to each lab.
- ◆ One sample collected from Town Brook - Cannonsville Reservoir watershed, Delaware County, NY
- ◆ 8 samples collected from streams within the Cannonsville Reservoir watershed.
- ◆ Samples transported to labs, refrigerated overnight - shipped next day

# Statistics

Labs rated based on a z-value, a non-parametric equivalent of a standard score (z-score).

$$z = \frac{X - \mu}{F\sigma}$$

$X$  = reported value

$\mu$  = sample median

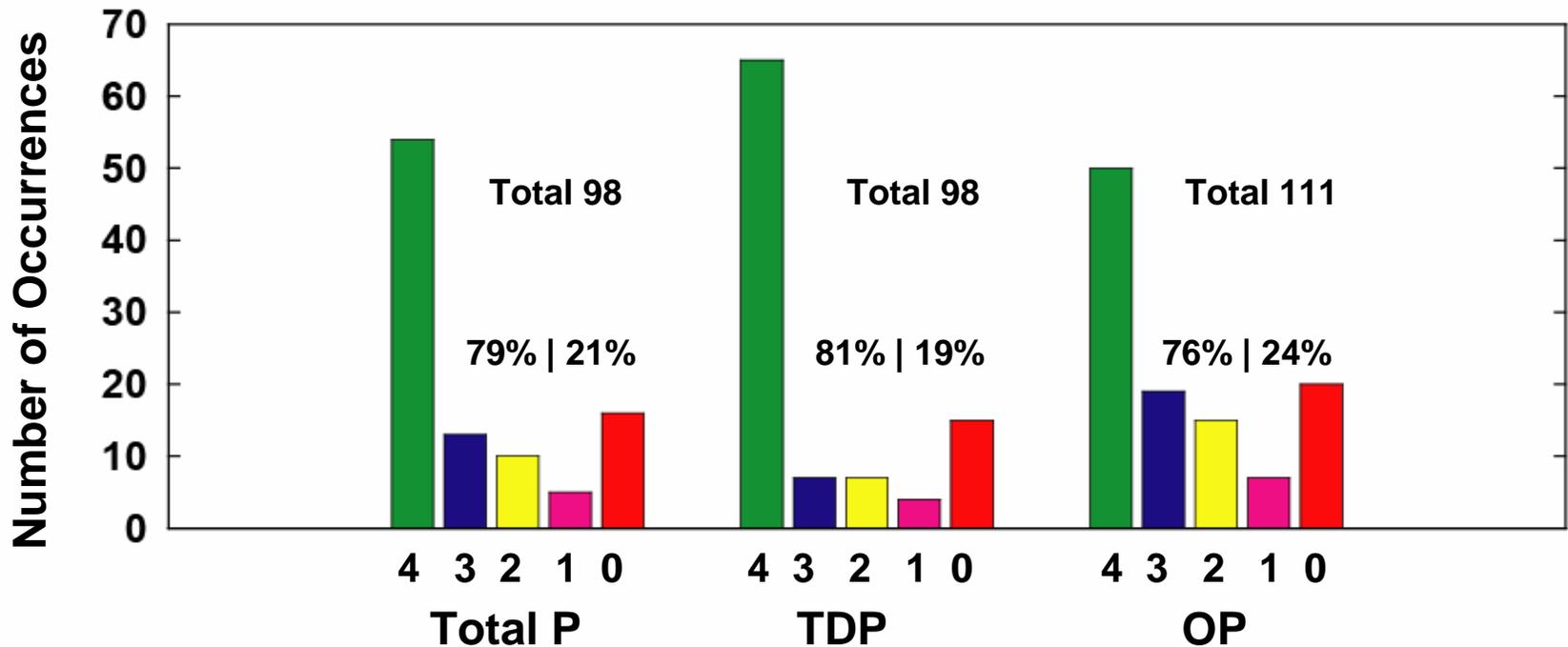
F-pseudosigma ( $F\sigma$ ) =  $(U_h - L_h)/1.349$

1.349 is equivalent to 2 standard deviations

# Ratings

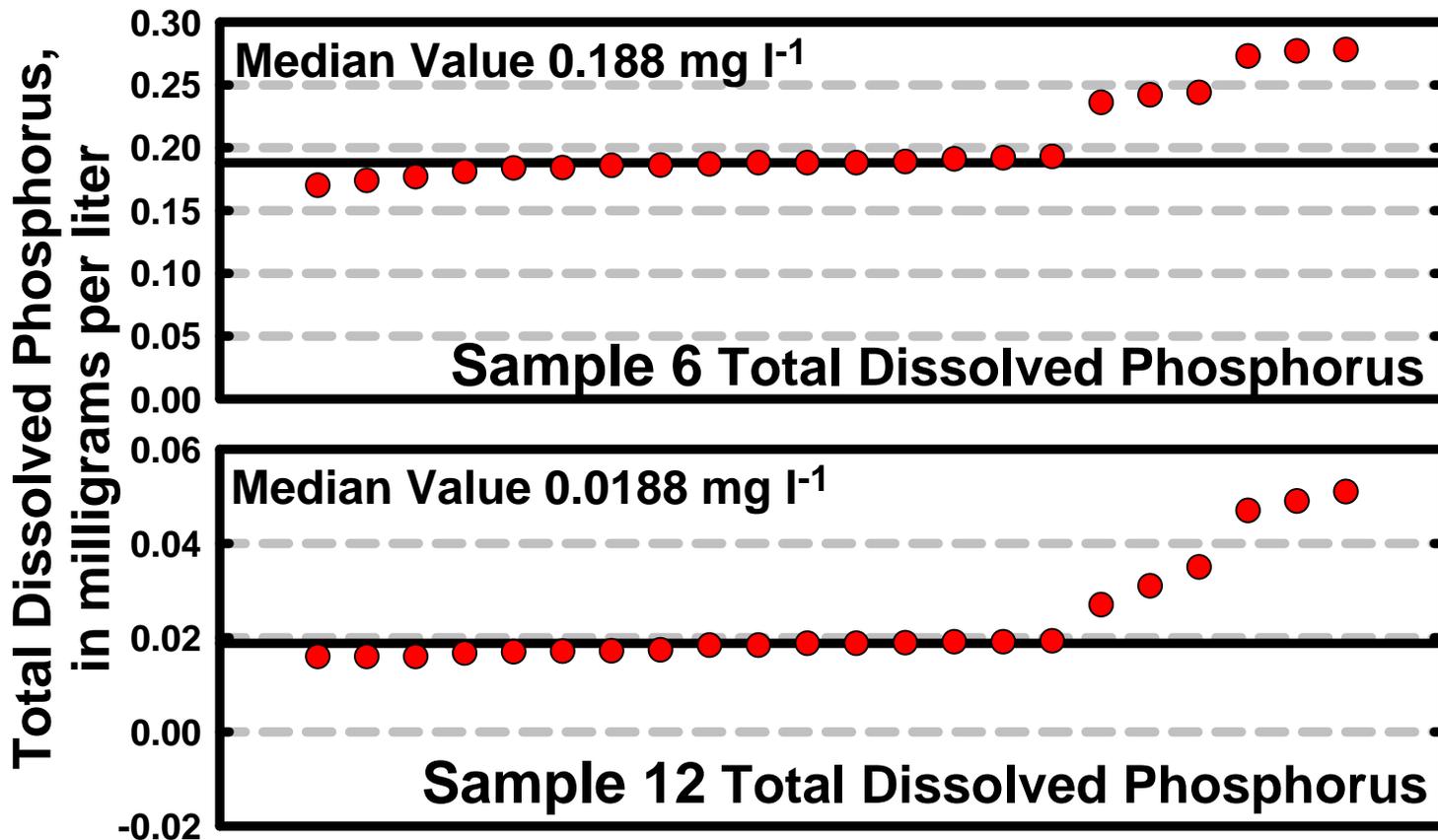
<b>Ratings</b>	<b>Absolute z-value</b>
<b>4 (Excellent)</b>	<b>0.00 to 0.50</b>
<b>3 (Good)</b>	<b>0.51 to 1.00</b>
<b>2 (Satisfactory)</b>	<b>1.01 to 1.50</b>
<b>1 (Marginal)</b>	<b>1.51 to 2.00</b>
<b>0 (Unsatisfactory)</b>	<b>Greater than 2.00</b>

# Summary of Lab Ratings for Rounds 1 and 2

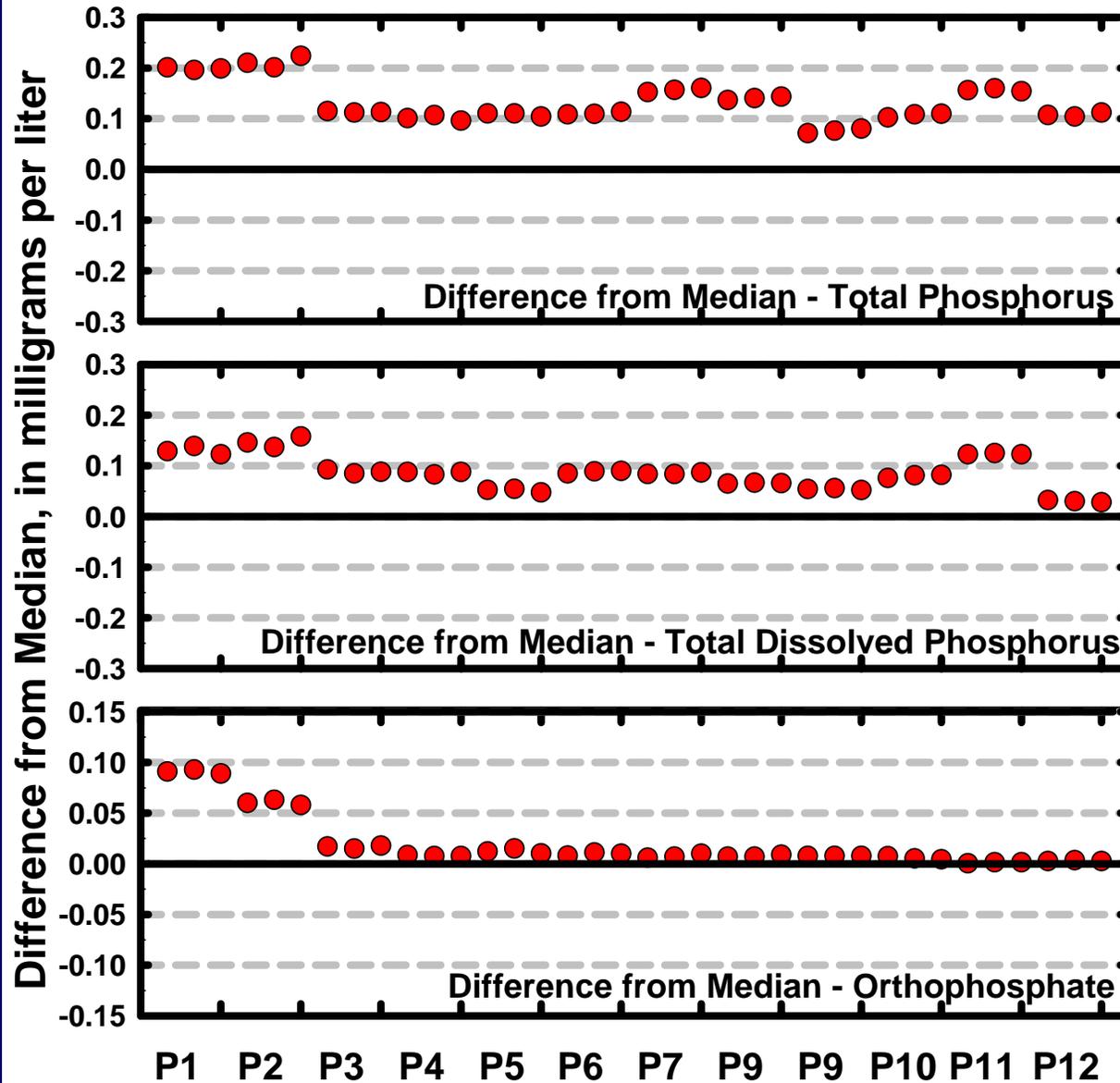




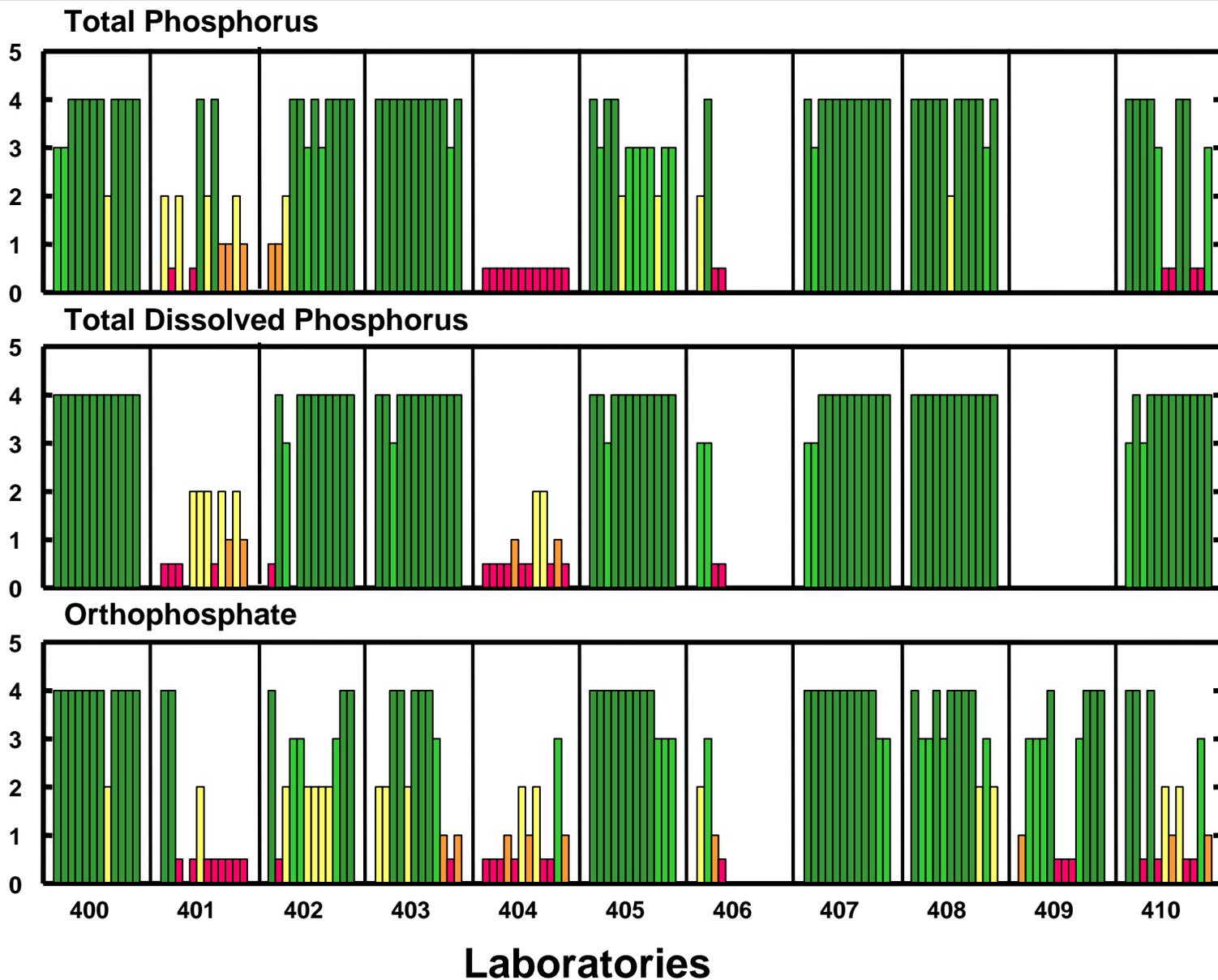
# Round 2 Results



# Laboratory Bias

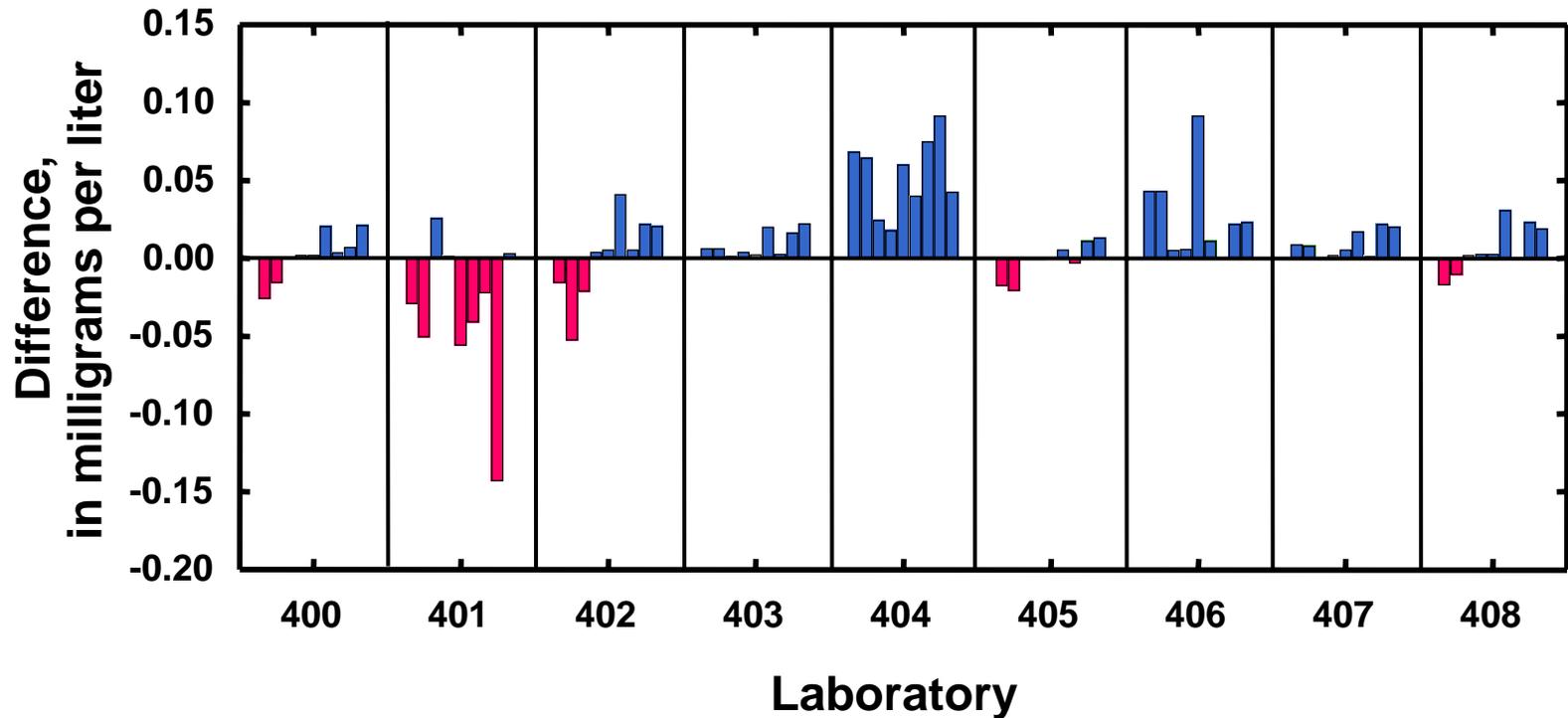


# Ratings between P species

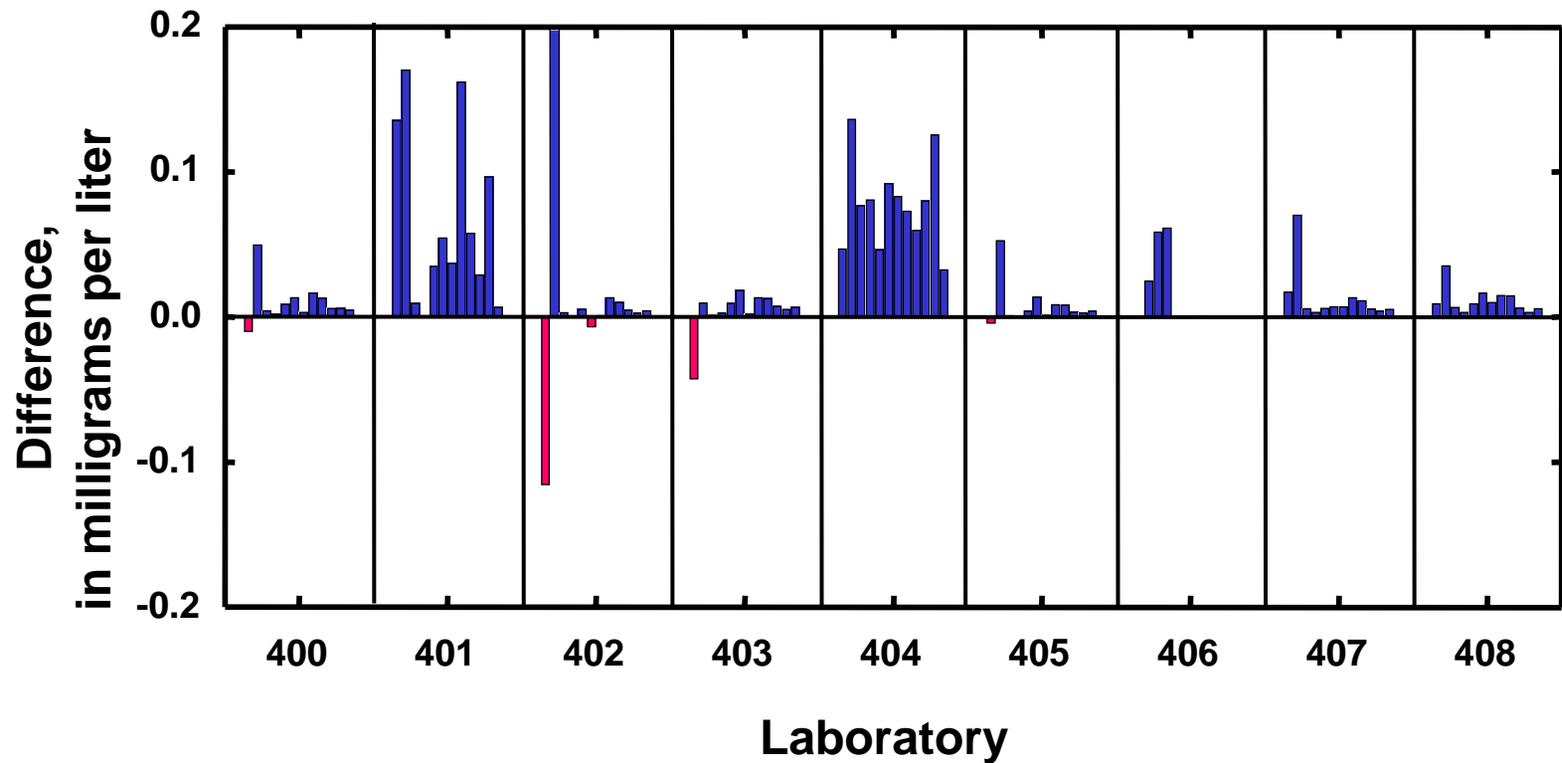


Performance Rating

# Total P minus Total Dissolved P



# Total Dissolved P minus Orthophosphate



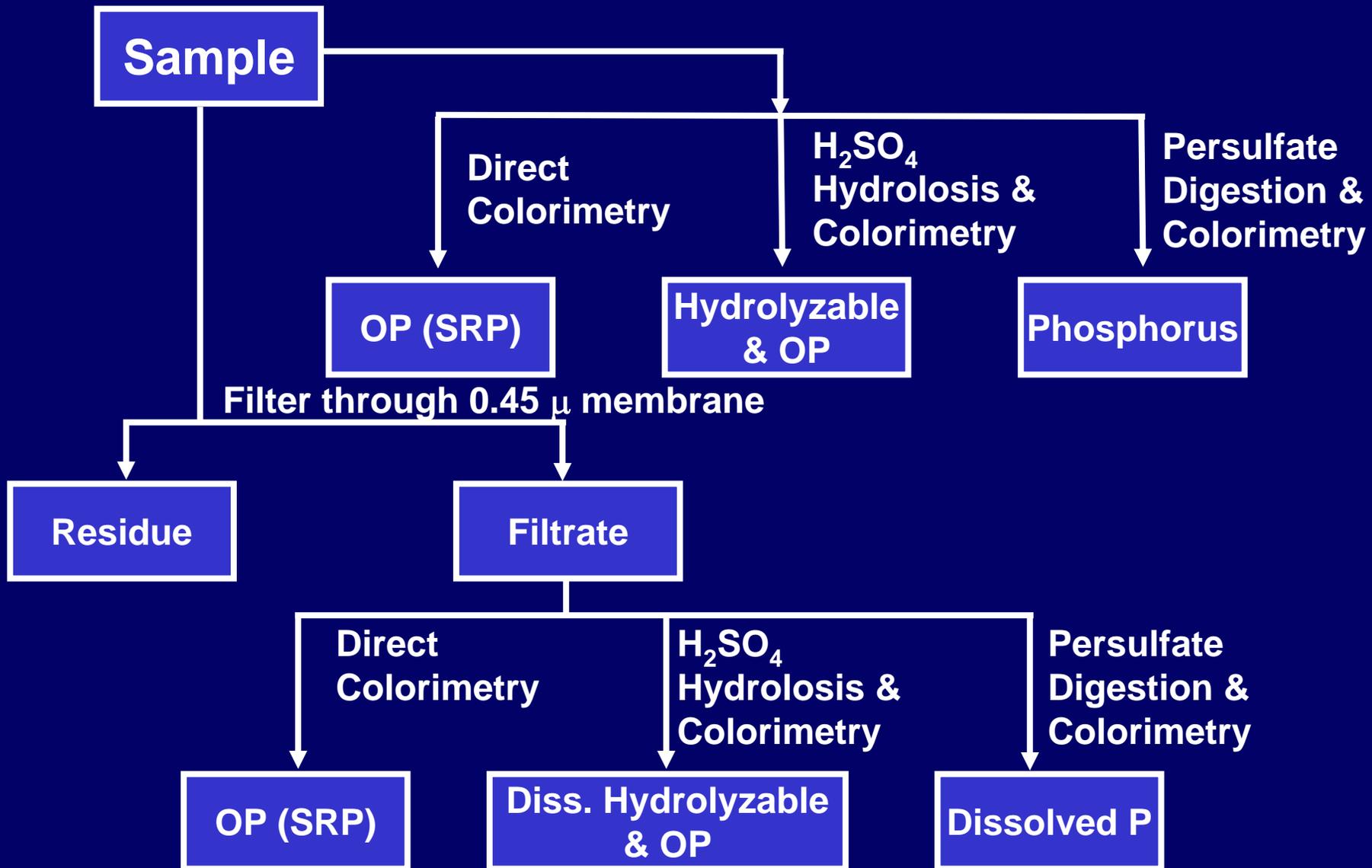
# EPA Methods Used

<b>USGS</b>	<b>365.1</b>
<b>CAS</b>	<b>365.1</b>
<b>UFI</b>	<b>365.2</b>
<b>NYS - DOH</b>	<b>365.3/365.2</b>
<b>Puerto Rico</b>	<b>365.1</b>
<b>NYC - DEP</b>	<b>365.1</b>
<b>STL</b>	<b>365.2</b>
<b>USDA</b>	<b>365.3/365.4</b>
<b>ANS</b>	<b>365.1</b>
<b>Cornell</b>	<b>365.1</b>

# Laboratory Methods

- Method 365.1: Phosphorus (All Forms, Colorimetric, Automated, Ascorbic Acid)
- Method 365.2: Phosphorus (All Forms, Colorimetric, Ascorbic Acid, Single Reagent)
- Method 365.3: Phosphorus (All Forms, Colorimetric, Ascorbic Acid, Two Reagent)
- Method 365.4: Phosphorus (Total, Colorimetric, Automated, Block Digester, AAI)

# Analytical Scheme for Differentiation of Phosphorus Forms EPA 365.1



# Comparison of Method 365.2

## Laboratory 1

- 5 ml of sample in two vials (total and hydrolyzed)
- Add  $K_2S_2O_8$
- Heat vials 30 min @ 150 °C
- Pipet 2 ml of 1.54N NaOH
- Add PhosVer3 Phosphate reagent
- Read on spectrophotometer at 890 nm

\*\* These methods do not include differences in calculation methods

## Laboratory 2

- 50 ml of sample
- Add 1 drop phenolphthalein
- Add  $H_2SO_4$  dropwise to discharge color
- Add 1 ml  $H_2SO_4$  and  $K_2S_2O_8$
- Boil gently 25-30 min or until final volume is 20 ml
- Dilute to 30 ml, add phenolphthalein, neutralize with NaOH
- Dilute to 100 ml separate to 2 vials add reagent to one run second as blank
- Read on spectrophotometer at 880 nm

# Conclusions

- ◆ **Lab's compared favorably well given the differences in methods**
- ◆ **Highlighted variability between & within methods**
- ◆ **Identified problems at some labs**
- ◆ **Raised questions regarding calculation of results (e.g. standard curve or a digested standard curve?)**

# Conclusions cont.

- **Although QA/QC samples and blanks provide information on precision, they do not provide information about laboratory accuracy.**
- **Results emphasize the need for labs to participate in regular PT study & sample exchange programs**

# Topics for Workshop Discussion

- 💧 **Should environmental samples be included in sample exchange programs?**
- 💧 **Statistics**
- 💧 **Methods comparability**
- 💧 **Laboratory Anonymity – is it important? Pros and cons**

# **Environmental Samples in Exchange Programs?**

- **Highly effective though potential for dissimilarity**
- **Digest/Extract exchange can refine evaluation of the causes of lab variability**

# Statistics

- **No issues identified, but must be valid for the analysis and data set(s)**

# Methods Comparability

- **Results of this study suggest questionable method comparability**
- **All methods generally provided excellent to fair precision**
- **Results suggest need for additional evaluation of true method comparability**

# Follow Up

- **USGS & Environment Canada PT's**
- **Additional Environmental Samples**
  - Ongoing evaluation of comparability
  - Determine whether study had +/- effect
- **Possibly Shared Digestates**

# Laboratory Anonymity

- **A BIG ISSUE!!!**
  - **Some labs insist it is essential**
  - **Others don't seem to care**

# Laboratory Anonymity, cont.

- **Pro:**
  - **Encourages willing participation**
- **Con:**
  - **Data users can't evaluate comparability**

# Laboratory Anonymity

- **The Solution!**
- **Put lab comparability FIRST**
  - **Ensure that lab data is comparable prior to analyzing project samples**
  - **Perform ongoing evaluations of capability & comparability**

# Disclaimer

**The views and opinions expressed  
are solely those of the  
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