Variability in Wastewater Effluent Phosphorus Measurements

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Seattle
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WERF Nutrients Challenge Goals

- Develop and share credible scientific information about nutrients & their bioavailability to help regulators make informed decisions
- Better understand existing mechanisms of nutrient removal and best available technologies so treatment plants can become more efficient and effective, enabling them to cost-effectively meet permit limits
  - Focus on nitrogen (N) and phosphorus (P)
  - Wastewater treatment related issues

- Status: Ongoing, 5 – 7 year challenge
- Investment: ~$3 million WERF funds (started in 2007)
- In-kind, in-cash: >$10 million
- Leveraged with additional funding, Collaboration, etc.

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Nutrient Removal Challenge
NUTR1R06 – Core Team

- Collaborative team led by HDR, with AECOM + CH2M-Hill + Univ. of Washington + other Universities + Collaborators
- >30 Utilities, Universities, Consultants, and Research Organizations nationwide and abroad
- Others added as needed
- Identified and secured >$10 million in additional funds or in-kind contributions through utilities & other research

Core Team and Other Members:

- JB Neethling, HDR (lead principal investigator)
- Julian Sandino, CH2M-Hill
- H. David Stensel, University of Washington
- Roy Tsuchihashi, AECOM
- David Clark, HDR

- Kartik Chandran, Columbia Univ
- Jacek Makinia, Gdansk Univ
- Stacy Passaro, Passaro

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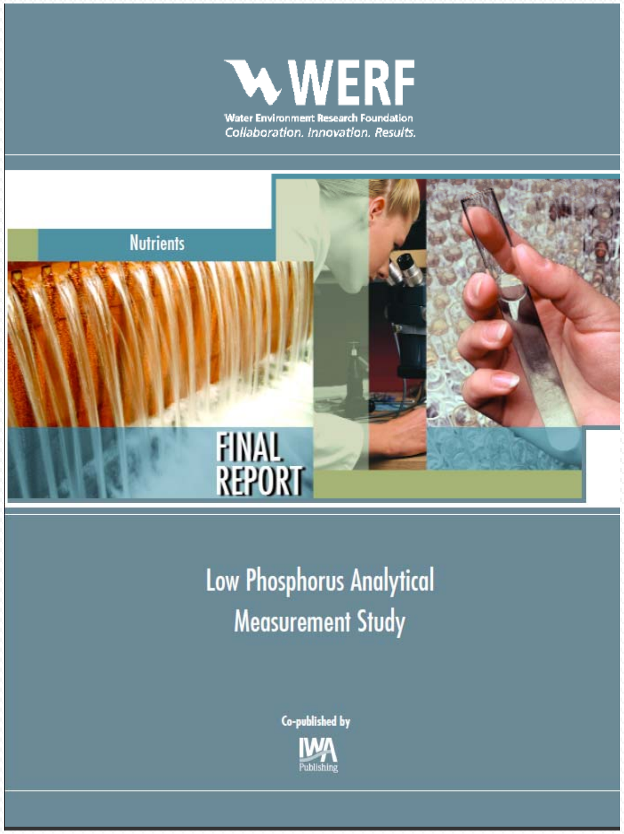
Outline

- Background and Motivation
- Methods
- Results and Discussion
- Third Study
- Significance of Speciation
- Conclusion
- Recommendations for Future Work
- Acknowledgements



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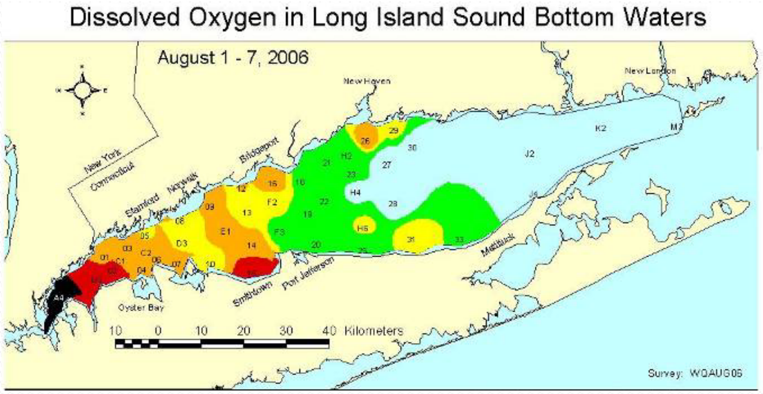
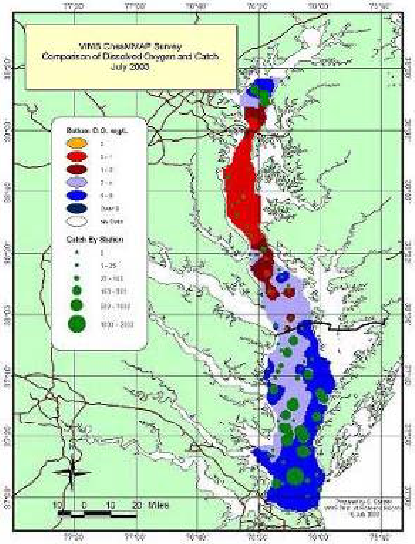
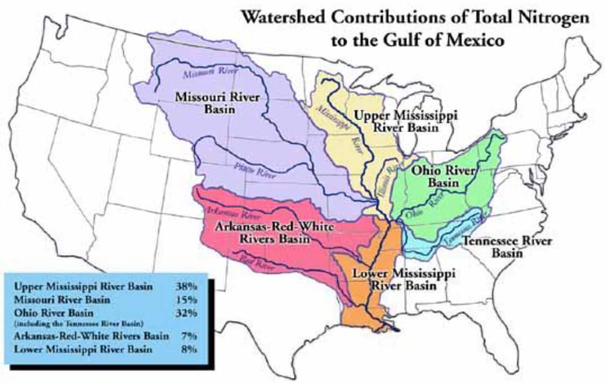
National Water Quality Priorities

Ben Grumbles, Former EPA Assistant Administrator for Water

- Chesapeake Bay
  - 150,000 new residents per year
- Gulf of Mexico
  - Large dead zone
  - Importance of phosphorus
- Long Island Sound
  - Below DO in half of sound
  - Water quality trading program implemented
- Puget Sound
  - Priority no. 1: Better handle on nutrient and bacteria loadings from septic systems







Several bills in Congress focused on water quality, including Chesapeake Bay, Long Island Sound, Lake Tahoe and Puget Sound

EPA's National Nutrient Strategy

- Nutrient Criteria Strategy, 1997
- EPA Develop Ecoregional Criteria
- States Develop Instream Standards
- States set Permit Limits (end-of-pipe)
- Without dilution, in-stream standard becomes end-of-pipe limits

Aggregate Ecoregions for Rivers and Streams

Parameter	Agg Ecor I	Agg Ecor II	Agg Ecor III	Agg Ecor IV	Agg Ecor V	Agg Ecor VI	Agg Ecor VII	Agg Ecor VIII	Agg Ecor IX	Agg Ecor X	Agg Ecor XI	Agg Ecor XII	Agg Ecor XIV
TP µg/L	47.00	10.00	21.88	23.00	67.00	76.25	33.00	10.00	36.56	128 *	10.00	40.00	31.25
TN mg/L	0.31	0.12	0.38	0.56	0.88	2.18	0.54	0.38	0.69	0.76	0.31	0.90	0.71

<u>Ecoregional Criteira are low:</u>

TP = 0.010-0.128 mg/L

TN = 0.12-2.18 mg/L

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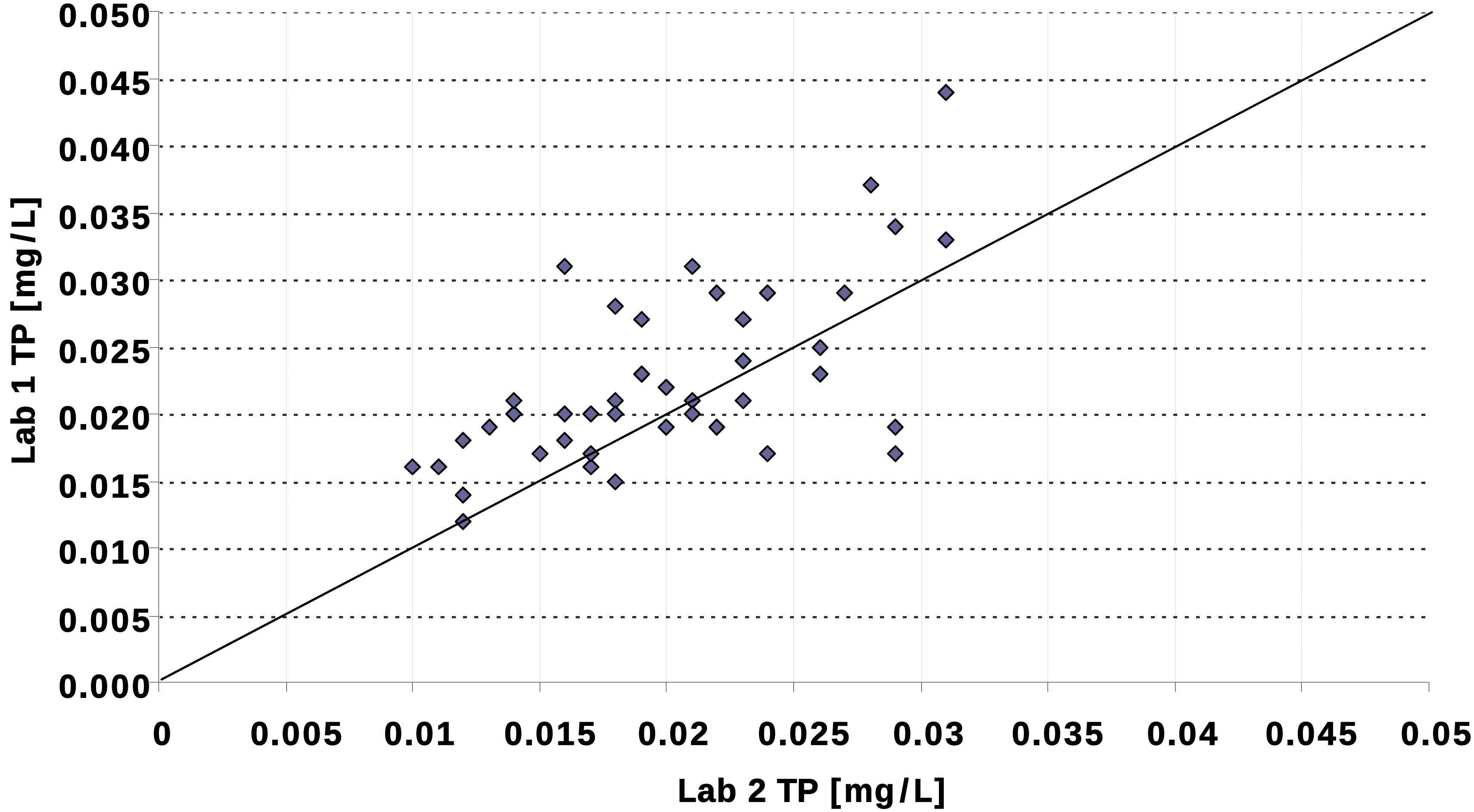
Background and Motivation

- Discharge requirements: extremely low P limits are required.
- Spokane river watershed TMDL
- Effluent TP ≤ 10 ug/L proposed; now 36 ug/L
- Pilots were conducted at:
  - City of Spokane, WA and Coeur d’Alene, ID
  - City of Las Vegas

Pilot Test #1 Laboratory Check



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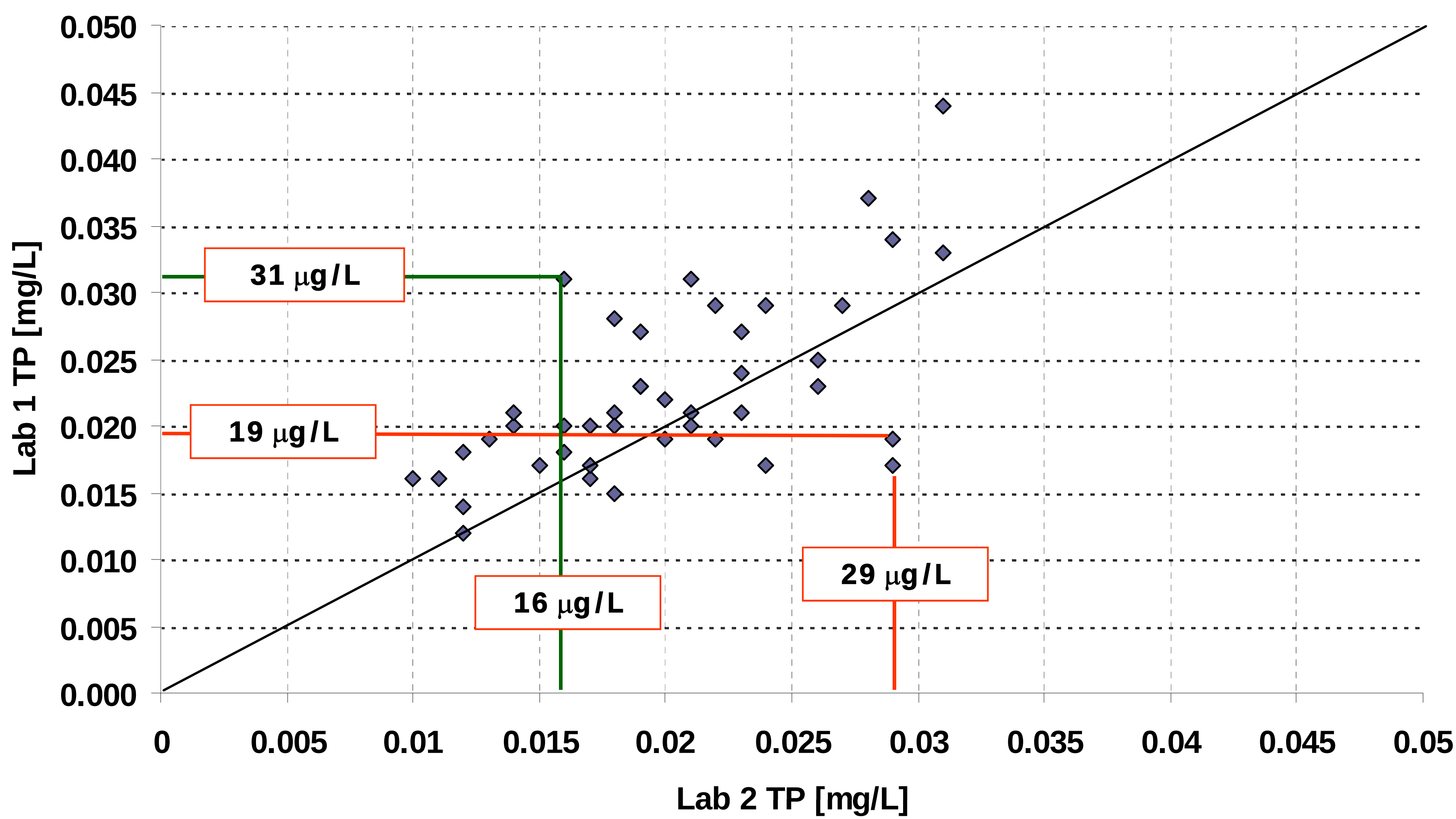
Pilot Test #2 Laboratory Check



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Objectives

- To determine P analysis reliability
- To document current certification programs
- To identify capable laboratories
- To present guidelines for future studies

Laboratory Survey - I

Lab	Method		Instrument		MDL ug/L		MRL ug/L	
	OP	**TP**	**OP**	**TP**	**OP**	**TP**	**OP**	**TP**
L 1	N/A	EPA 365.1	Spectrophoto-meter		N/A	1	N/A	5
L 2	SM4500 -PE	SM4500 -PE	Spectrophoto-meter		2	5	10	10
L 3	SM4500 -PE	SM4500 -PE	Spectrophoto-meter		2	2	10	1
L 4	EPA 365.1	EPA 365.1	AFI		0.22	1.4	2	10
L 5	SM4500 -PE	EPA 365.3	Spectrophoto-meter		0.4	0.62	1	1

AFI – Automated Flow Injection SFA – Segmented Flow Analyzer

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Laboratory Survey - II

Lab	Method		Instrument		MDL ug/L		MRL ug/L	
	OP	TP	OP	TP	OP	TP	OP	TP
L 6	SM4500-PE	SM4500-PE	OI Analyzer		2	2	2	2
L 7	SM4500-PF	SM4500-PE	SFA	Spectro.	0.5	2	1	2
L 8	SM4500-PE	SM4500-PE	Spectrophoto-meter		1.5	1.5	2	2
L 9	SM4500-PE	SM4500-PE	OI Analytical Segment		N/A	N/A	2	20
L 10	EPA 365.2	EPA 365.4	Spectrophoto-meter		3	4	4	N/A

AFI – Automated Flow Injection   SFA – Segmented Flow Analyzer

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Laboratory Survey

- Modifications to the Methods:
  - Increased sensitivity: 660 – 880 nm
  - Longer cuvettes
  - Increased cell path

- Accreditation:
  - 5 labs are accredited by state agency
  - 2 labs are accredited by NELAC
  - 3 labs are not accredited

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Experimental Design

- Total of 12 samples (duplicates of 6 different samples)
- Samples Matrixes:
  - 18 MΩ deionized water
  - Wastewater tertiary effluent
- Samples Modifications:
  - Blank samples spiked with 3 mg/L and 6 mg/L of orthophosphate
  - WW effluent diluted with filtered Lake Mead water
- TP & OP conc. in the WW effluent samples:
  - TP & OP conc. were measured in the WW effluent and filtered Lake Mead water samples.
  - WW effluent Dilutions:
    - 80% Lake Mead + 20% WW effluent
    - 95% Lake Mead + 5% WW effluent

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Samples Description

ID	Description	Dilute with	DF	Spike, mg/L	LW%	Efflu-ent %	OP, ug/L	TP, ug/L
A1	WWTE	LW	5	0	80%	20%	6.2	18.3
C1	WWTE	LW	5	0	80%	20%	6.2	18.3
A2	WWTE	LW	20	0	95%	5%	2.7	10.5
C2	WWTE	LW	20	0	95%	5%	2.7	10.5
A3	WWTE	LW	20	6			8.7	16.5
C3	WWTE	LW	20	6			8.7	16.5
B1	Blank						0.0	0.0
D1	Blank						0.0	0.0
B2	DI			3			3.0	3.0
D2	DI			3			3.0	3.0
B3	DI			6			6.0	6.0
D3	DI			6			6.0	6.0

WWTE - Wastewater Tertiary Effluent; LW - Lake Mead water; DF – Dilution factor

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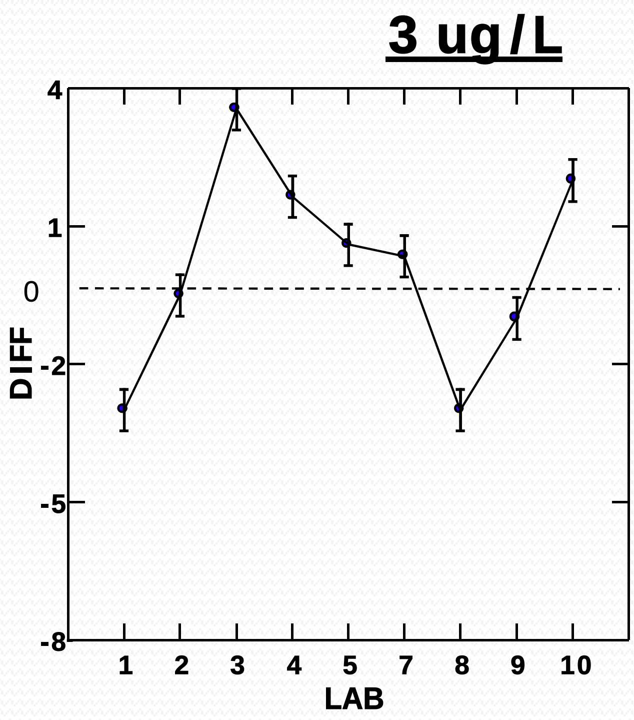
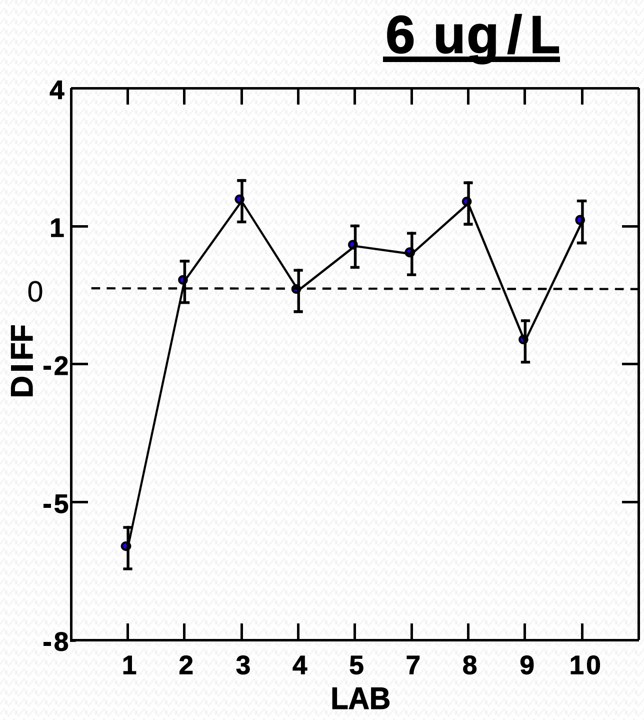
TP Measurements Variability in 18 MΩ DI





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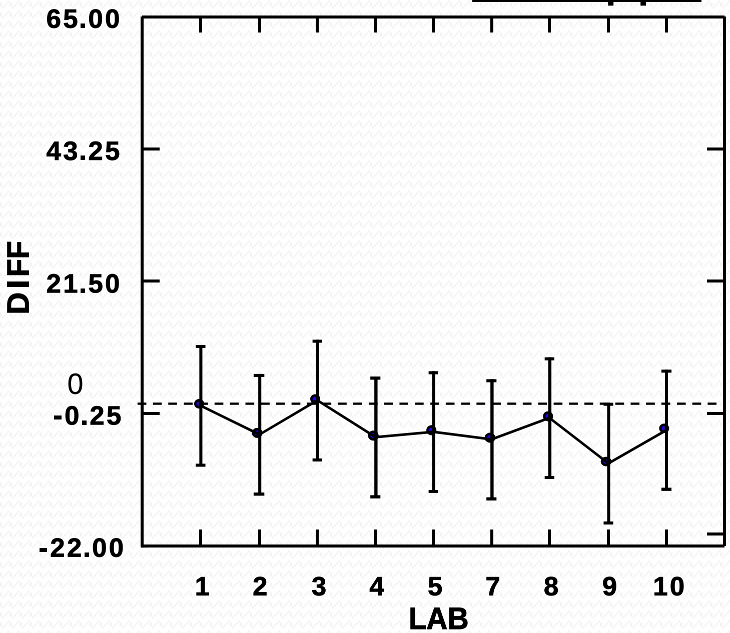
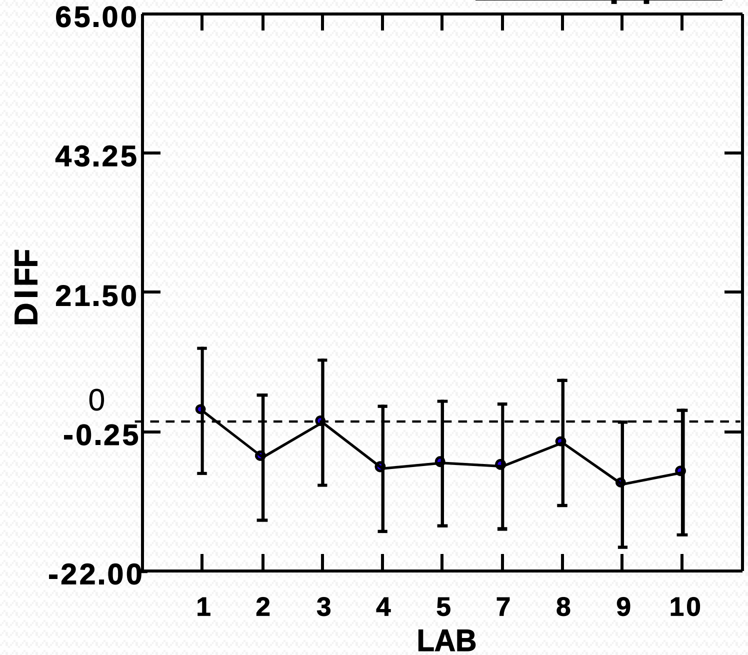
TP Measurements Variability in the WW Effluent

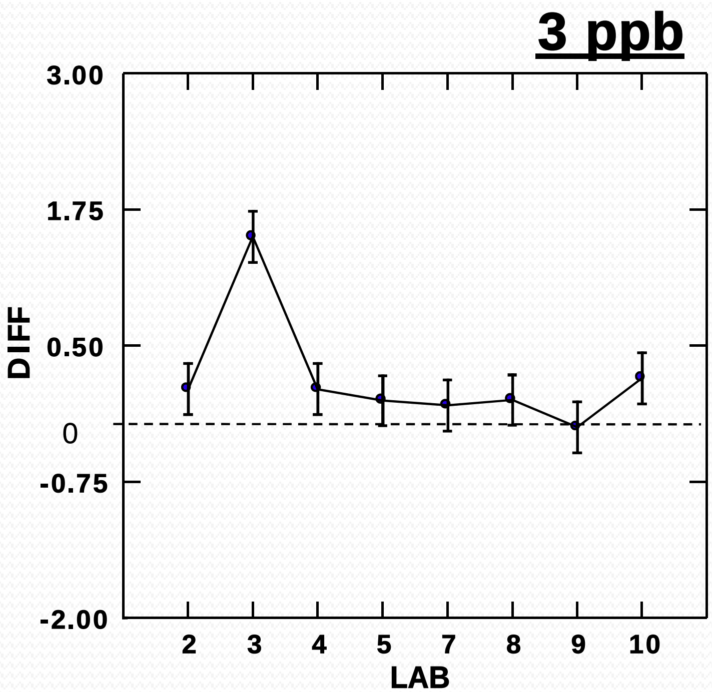
10.5 ppb

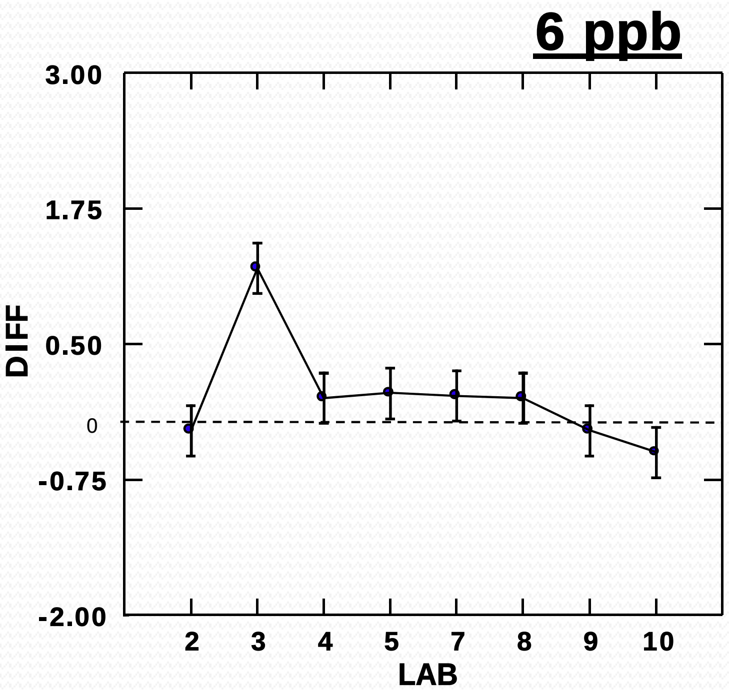


16.5 ppb



OP Measurements Variability in 18 MΩ DI





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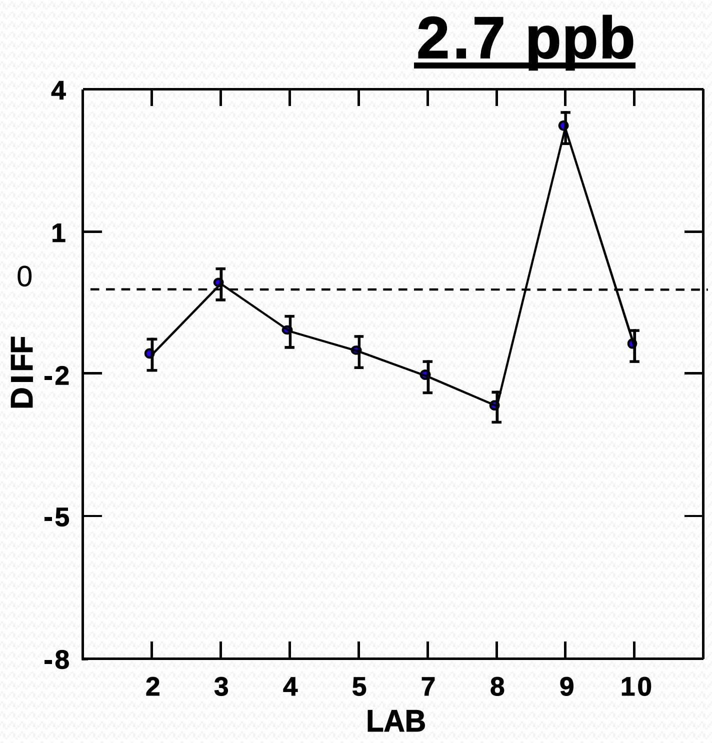
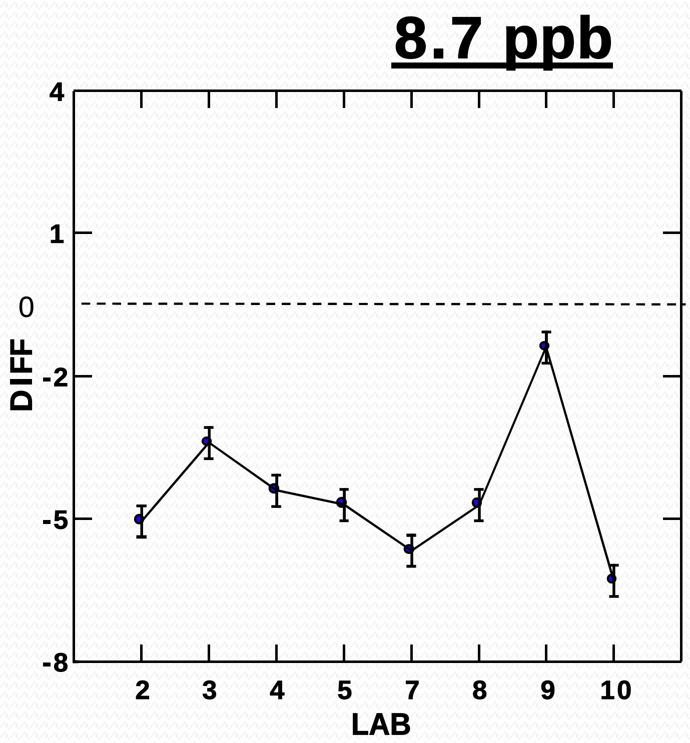
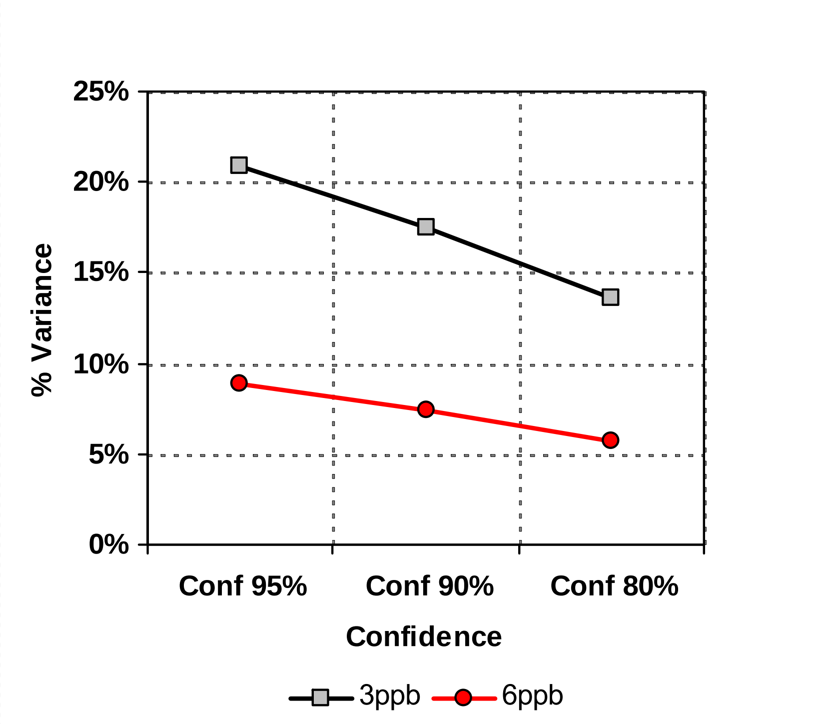
OP Measurements Variability in WW Effluent

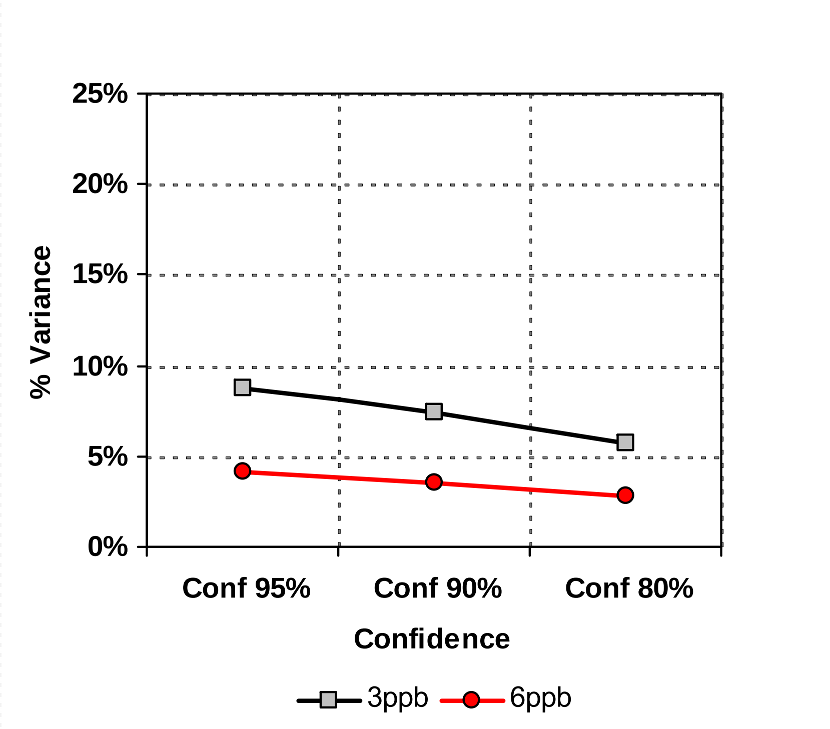




Variance

- Comparison TP and OP in DI Water





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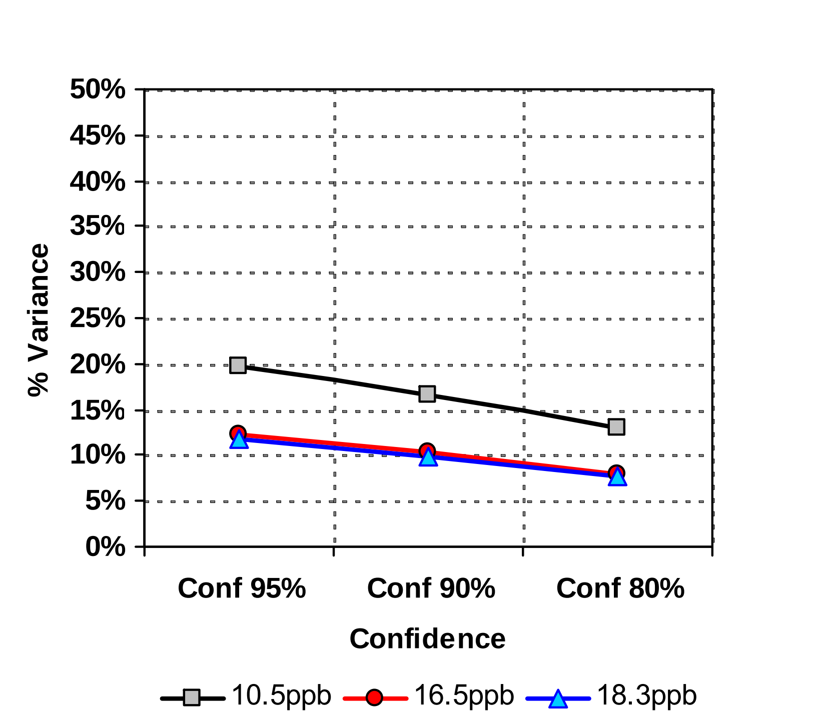
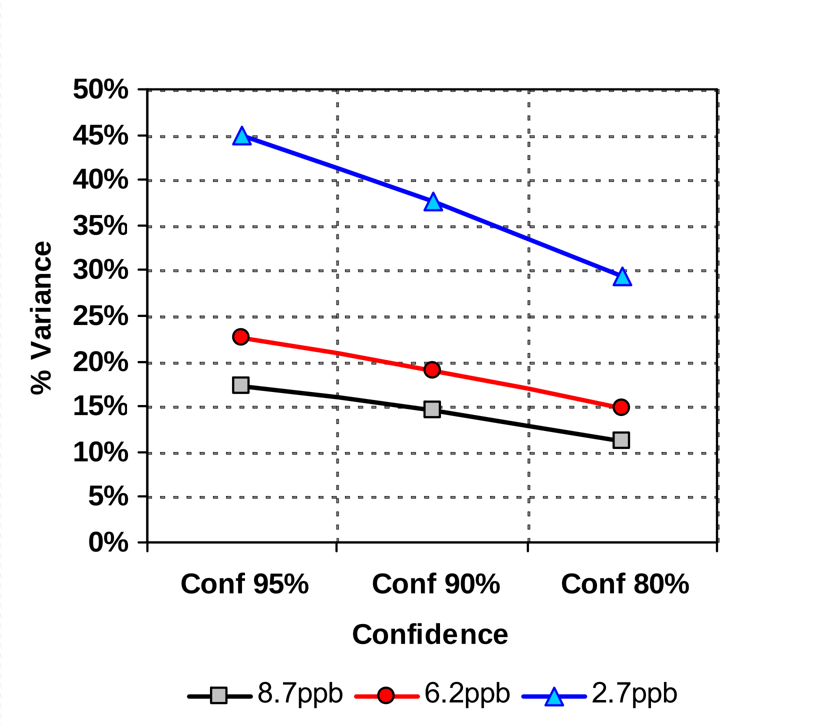
Variance

- Comparison TP and OP in WW Effluent





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Spike Recovery – Blank Sample

	Spike	Value	2	3	4	5	7	8	9	10
Mean	3	3	3.1	4.5	3.1	3	2.9	3	2.8	3.2
Recovery	3	3	2.9	2.4	2.2	2.8	2.9	3	2.6	1.5
% Recovery		100%	97%	80%	72%	95%	97%	100%	85%	50%

	Spike	Value	2	3	4	5	7	8	9	10
Mean	6	6	5.7	7.2	6	6	6	6	5.7	5.5
Recovery	6	6	5.5	5.1	5.1	5.9	6	6	5.5	3.8
% Recovery		100%	92%	85%	84%	98%	100%	100%	92%	63%

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Spike Recovery – Effluent sample

	Spike	Value	2	3	4	5	7	8	9	10
Mean	6	8.7*	3.7	5.3	4.3	4	3	4	7.3	2.4
Recovery	6	6	2.6	2.7	2.7	2.8	2.4	4	1.4	1.1
% Recovery		100%	43%	45%	45%	47%	39%	67%	23%	18%

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Third Pilot Methods Evaluation

- Used 4 laboratories
- Three methods
  - Colorimetric
  - ICP
  - ICP/MS
- Samples
  - Spike Deionized Water
  - Spiked Treated Effluent
    - 5 ug/L
    - 10 ug/L

Third Pilot Method Evaluation

Lab	A	D	C	B	A	D	B	D
Method	Ac Acid EPA 365.3	Auto Asc Acid SM 4500PF	SM 4500 PE	ICP EPA 200.7	ICP EPA 200.7	ICP EPA 200.7	ICP/MS EPA 200.8	ICP/MS Agilent 7500
DI+5								
Average	5.5	4.9	5.62	7.35	3.8	7.84	5.73	14
St Dev	0.3	1.4	0.251	1.81	1.4	1.75	0.358	0.4
Coeff Var	5.5	28.6	4.5	9.2	27	22.3	6.2	2.9
%Recov	110	98	112	147	76	157	115	280
QA1								
Average	19.9	43.3	15.5	17	17.3	17.4	14.8	20.2
St Dev	4.8	0.2	0.33	1.69	3.3	4	0.239	0.4
Coeff Var	24.1	0.46	2.1	9.9	12.7	23	1.6	2
QA1+5								
Average	22.5	42.4	20.4	21.6	22.9	22.6	19.4	24.8
St Dev	2.1	0.8	0.31	3.39	0.9	2.6	0.3	0.3
Coeff Var	9.3	1.9	1.52	15.7	3.9	11.5	1.55	1.21
%Recov	52	0	98	92	112	104	92	92
QA1+10								
Average	27.5	48.7	26.2	28.7	27.7	29	25.5	32.2
St Dev	2	0.8	0.135	1.47	1.4	3.1	0.72	0.4
Coeff Var	7.3	1.6	0.51	5.1	5.1	10.7	2.8	1.2
%Recov	76	54	107	117	104	116	107	120

Ref. (Analysis by D. Jenkins, 2010)

Criteria: CoVar <20%; Spike recovered 80-120%

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Third Pilot Methods Finding

- Lab Technique Practice plays a role – even when using the same method, the results are not consistent
- Low concentrations – 5 ug/L in distilled water, results are mixed, generally poor
- Higher concentrations (15-30 ug/L) the ICP and ICP/MS appears to do better.
- Good laboratory analysis are able to recover the small spike with high accuracy – meeting the 80-120% recovery threshhold.

- <u>Message:</u> If the laboratory can recover a small spike (same order of magnitude as the measured result), then the result is likely good.

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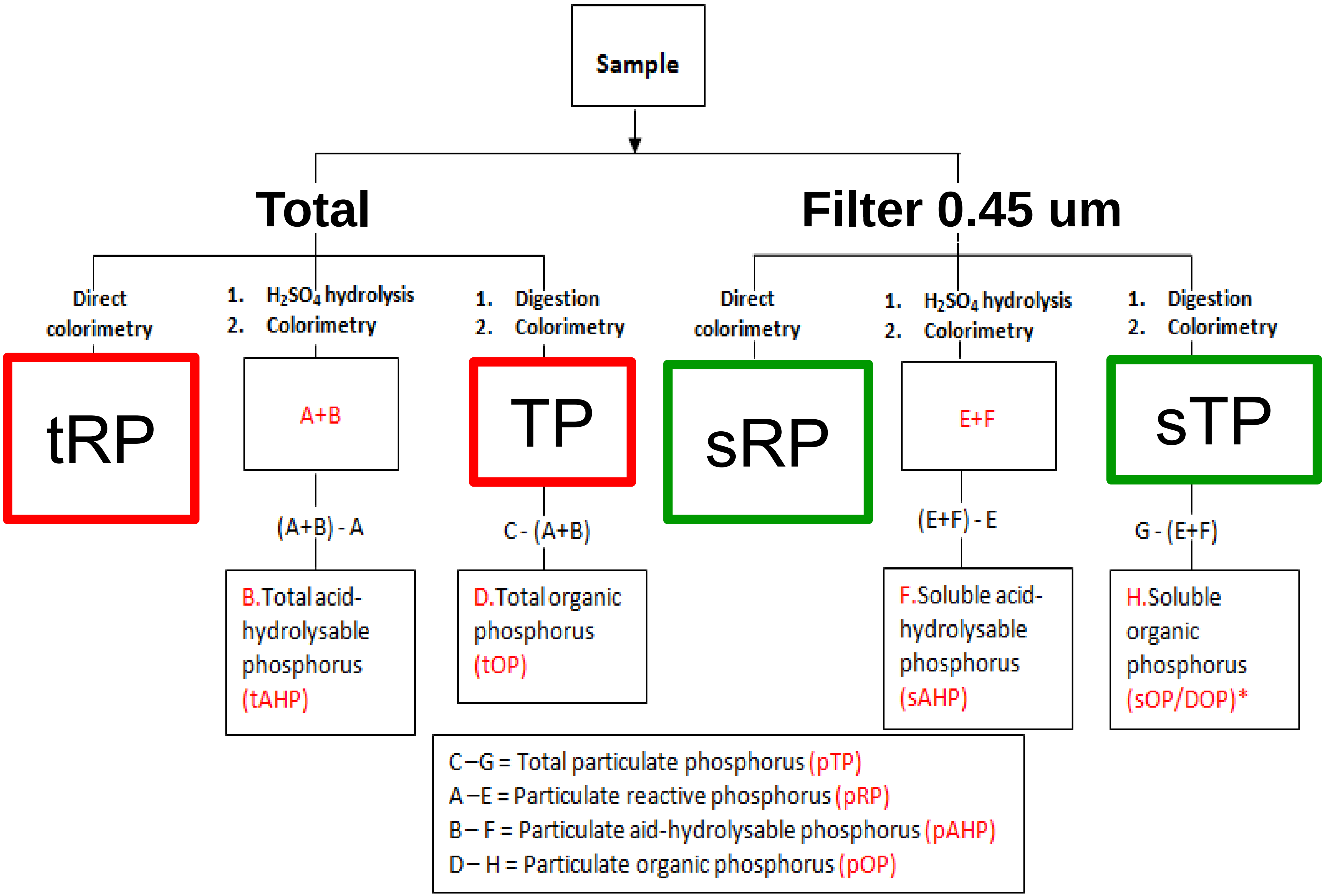
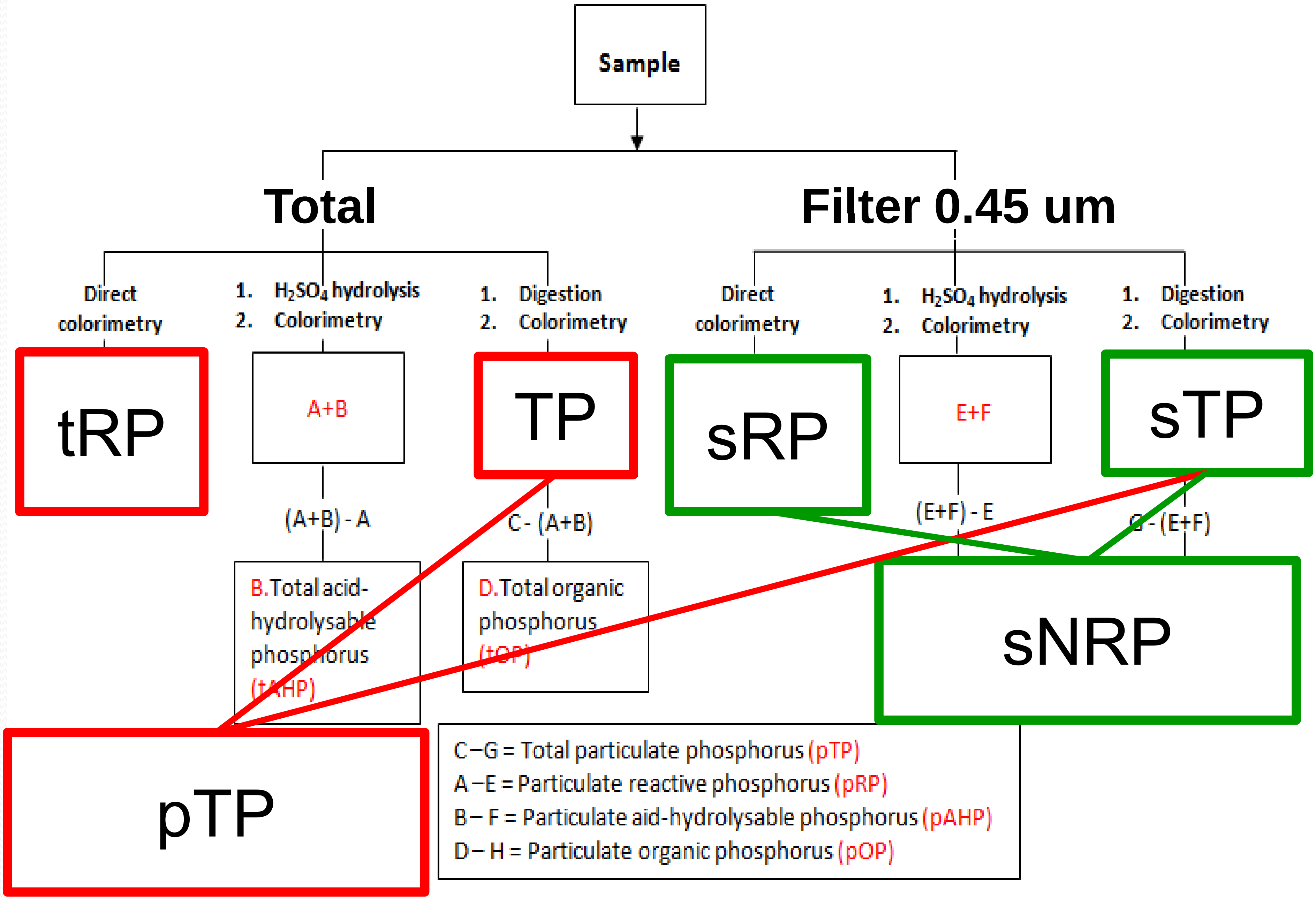
P Fractions

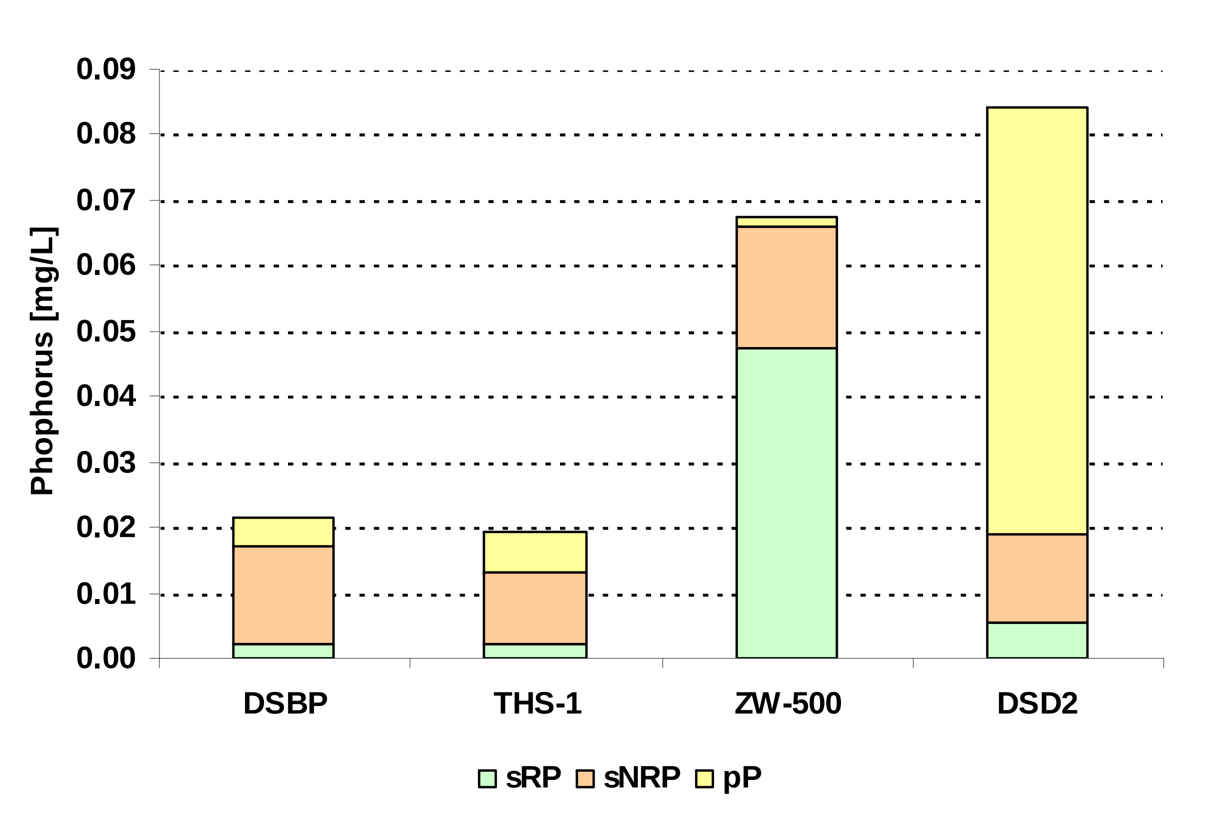

Sample
Total
Filter 0.45 um
Direct colorimetry
1. H2SO4 hydrolysis
2. Colorimetry
1. Digestion
2. Colorimetry
Direct colorimetry
1. H2SO4 hydrolysis
2. Colorimetry
1. Digestion
2. Colorimetry
tRP
A+B
TP
sRP
E+F
sTP
(A+B) - A
C - (A+B)
(E+F) - E
G - (E+F)
B.Total acid-hydrolysable phosphorus (tAHP)
D.Total organic phosphorus (tOP)
F.Soluble acid-hydrolysable phosphorus (sAHP)
H.Soluble organic phosphorus (sOP/DOP)*
C−G = Total particulate phosphorus (pTP)
A−E = Particulate reactive phosphorus (pRP)
B− F = Particulate aid-hydrolysable phosphorus (pAHP)
D− H = Particulate organic phosphorus (pOP)

P Fractions

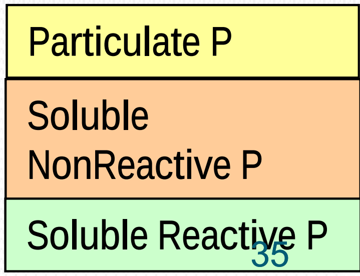


Sample
Total
Filter 0.45 um
Direct colorimetry
1. H2SO4 hydrolysis
2. Colorimetry
1. Digestion
2. Colorimetry
tRP
A+B
TP
sRP
E+F
sTP
(A+B) - A
C - (A+B)
(E+F) - E
G - (E+F)
B. Total acid-hydrolysable phosphorus (tAHP)
D. Total organic phosphorus (tOP)
sNRP
pTP
C−G = Total particulate phosphorus (pTP)
A−E = Particulate reactive phosphorus (pRP)
B− F = Particulate aid-hydrolysable phosphorus (pAHP)
D− H = Particulate organic phosphorus (pOP)

Pilot Study Results Illustrated Importance of Species



- No Treatment Technology Available for Soluble Non-Reactive P
- Portion May Not Be Bioavailable



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Future Work

- Identify source of variability: instrument, methods, interferences, human factor
- Develop new methods and/or guidelines for low P analysis
- Investigate opportunities for collaboration to develop new methods

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Acknowledgements

- Funding:
  - City of Coeur d'Alene
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  - Analytical Sciences Lab – Holm Research Center, Univ. of Idaho
  - City of Coeur d'Alene WWTP Laboratory
  - City of Las Vegas Environmental Division Laboratory
  - City of Spokane RPWRF Laboratory
  - Clark County Water Reclamation District Laboratory
  - High Sierra Water Laboratory
  - Lower Colorado Regional Laboratory
  - SVL Analytical, Inc.
  - Southern Nevada Water Authority Laboratory
  - Weck Laboratories

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