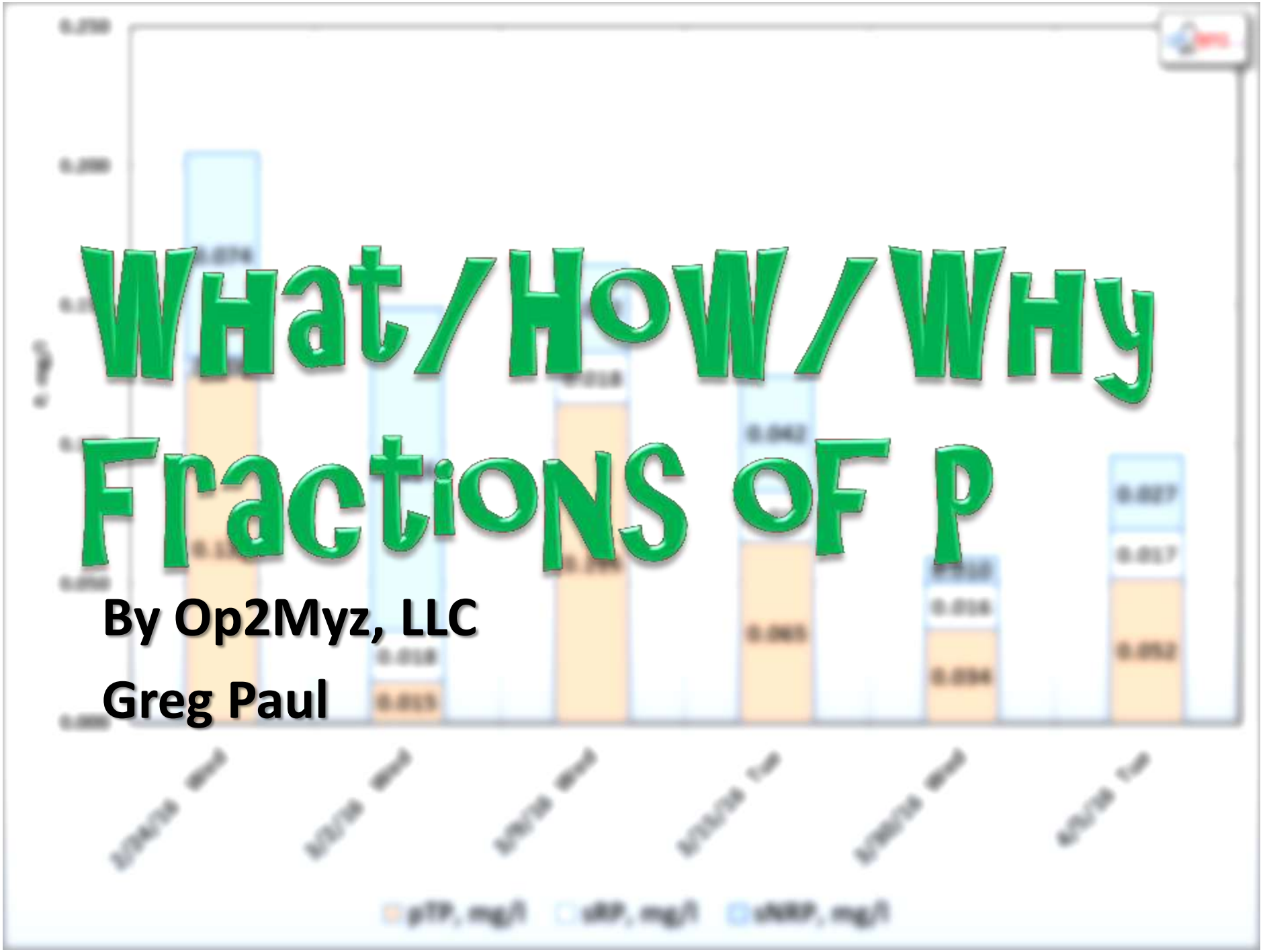


What/How/Why Fractions of P

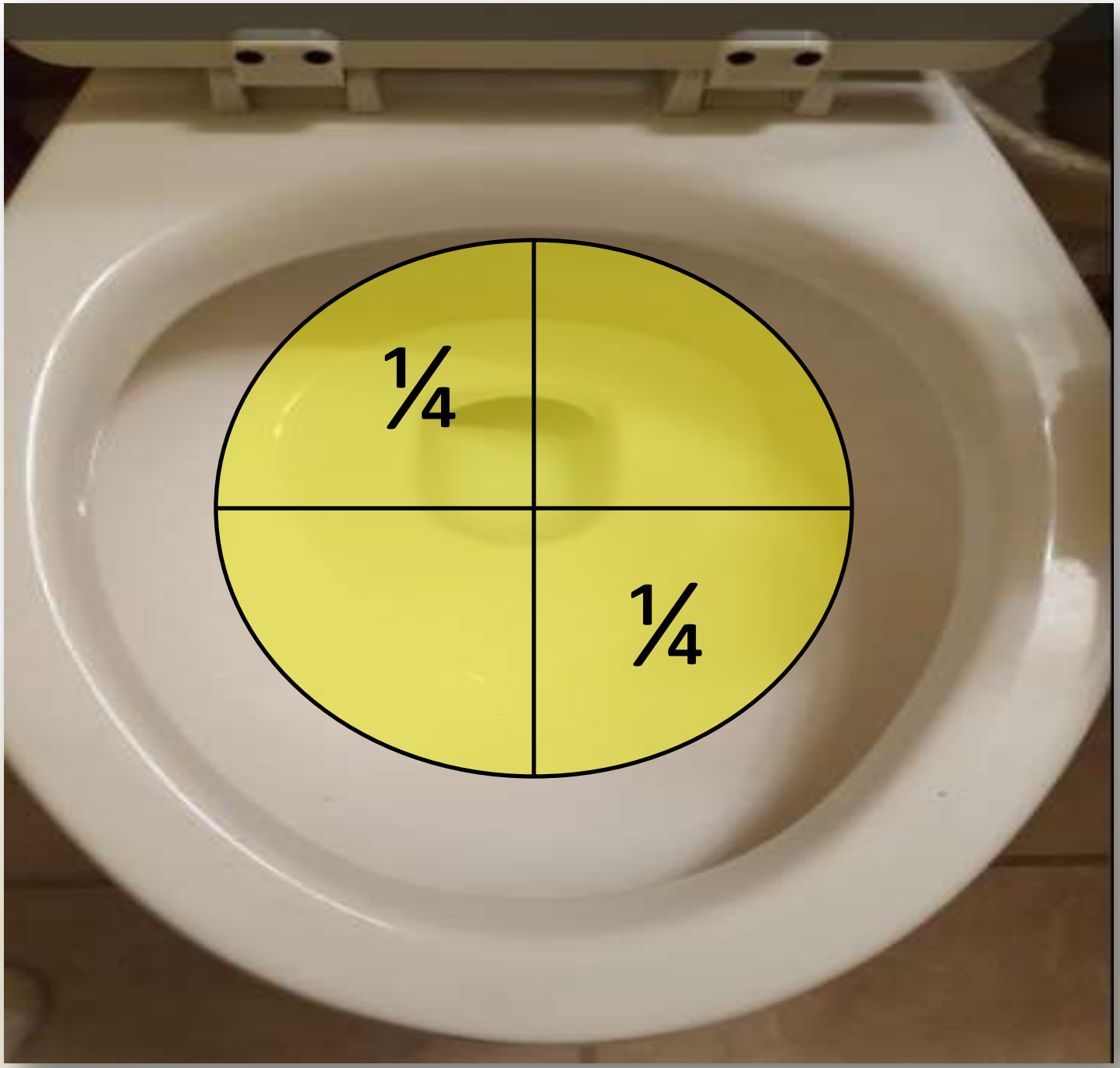
By Op2Myz, LLC

Greg Paul

What

ARE

FRACTIONS OF P ???



Fractions of P

Fractions of “Phosphorus”

OF Course

Everything is ABOUT

Phosphorus These Days

What are the Fractions P ?

- What are Fractions of P - Sometimes called P "species"?

Total Phosphorus is just that →

- The **total** OF the **DIFFERENT** Phosphorus FRACTIONS or SPECIES
- There are numerous DIFFERENT type of Phosphorus which all together make up TOTAL PHOSPHORUS

Four Ways to Characterize P

- Reactive Phosphorus
- Non-Reactive Phosphorus
- Soluble Phosphorus
- Particulate Phosphorus
- 5th – Acid Hydrolysable (dissolve in acid) – part of more complex fractions

Simpler Fractions of P

- Total Phosphorus can be fractionalized into 4 **basic** parts,
  - 2 of the fractions come directly from analysis sTP & sRP
  - The other two, pTP & sNRP, are calculated using the results of 3 different analyses, sTP, sRP and TP

Putting it All Together

Simpler Fractions of P

- Total Phosphorus (**TP**)
- Total Soluble Phosphorus (**sTP**)
  - Filtered TP
- Soluble Reactive Phosphorus (**sRP**)
  - Filtered ortho-P
- Soluble Non-Reactive Phosphorus (**sNRP**)
  - sTP minus sRP
- Particulate Total Phosphorus (**pTP**)
  - TP minus sTP

How do

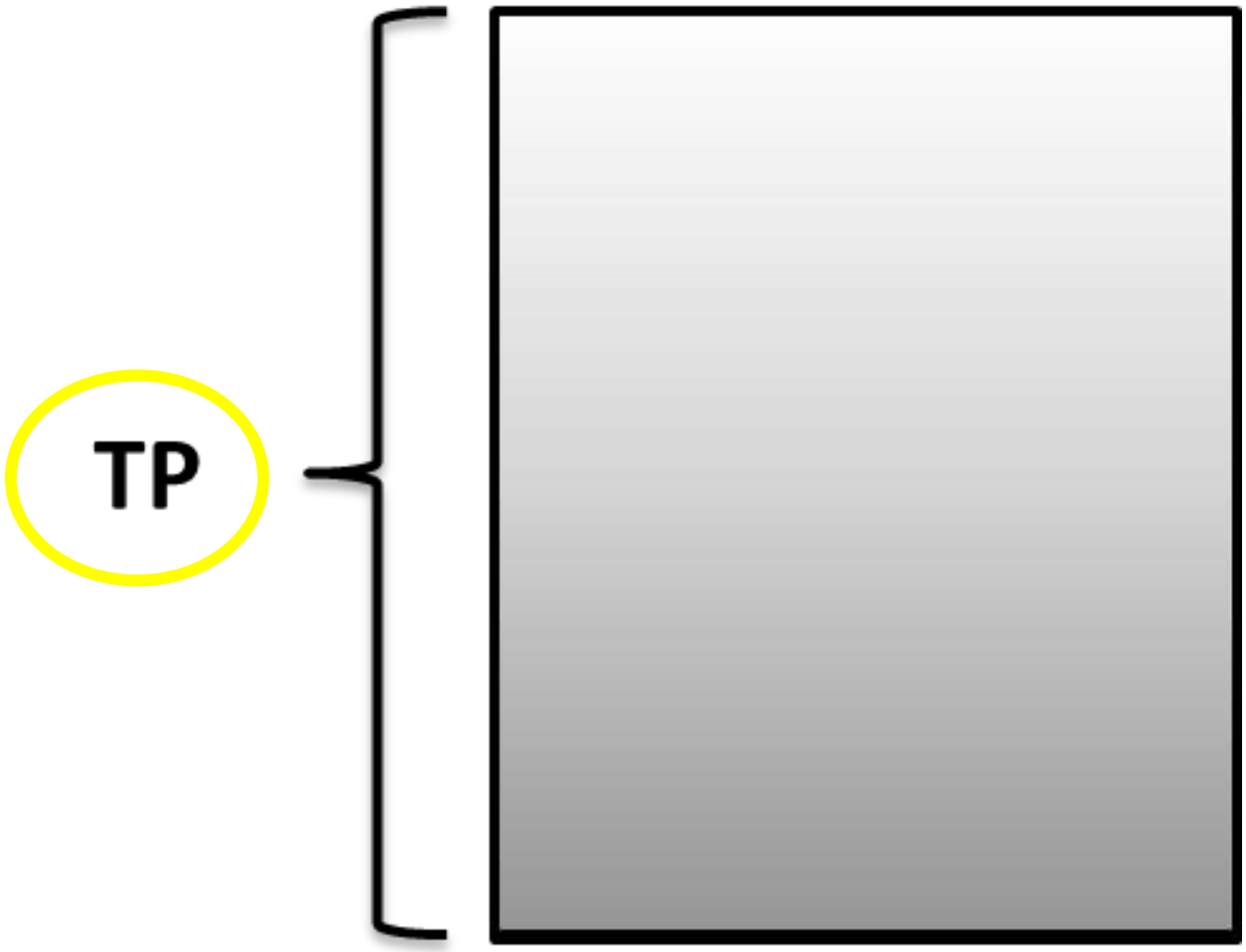
get the Simpler

FRACTIONS OF P ???

Total Phosphorus

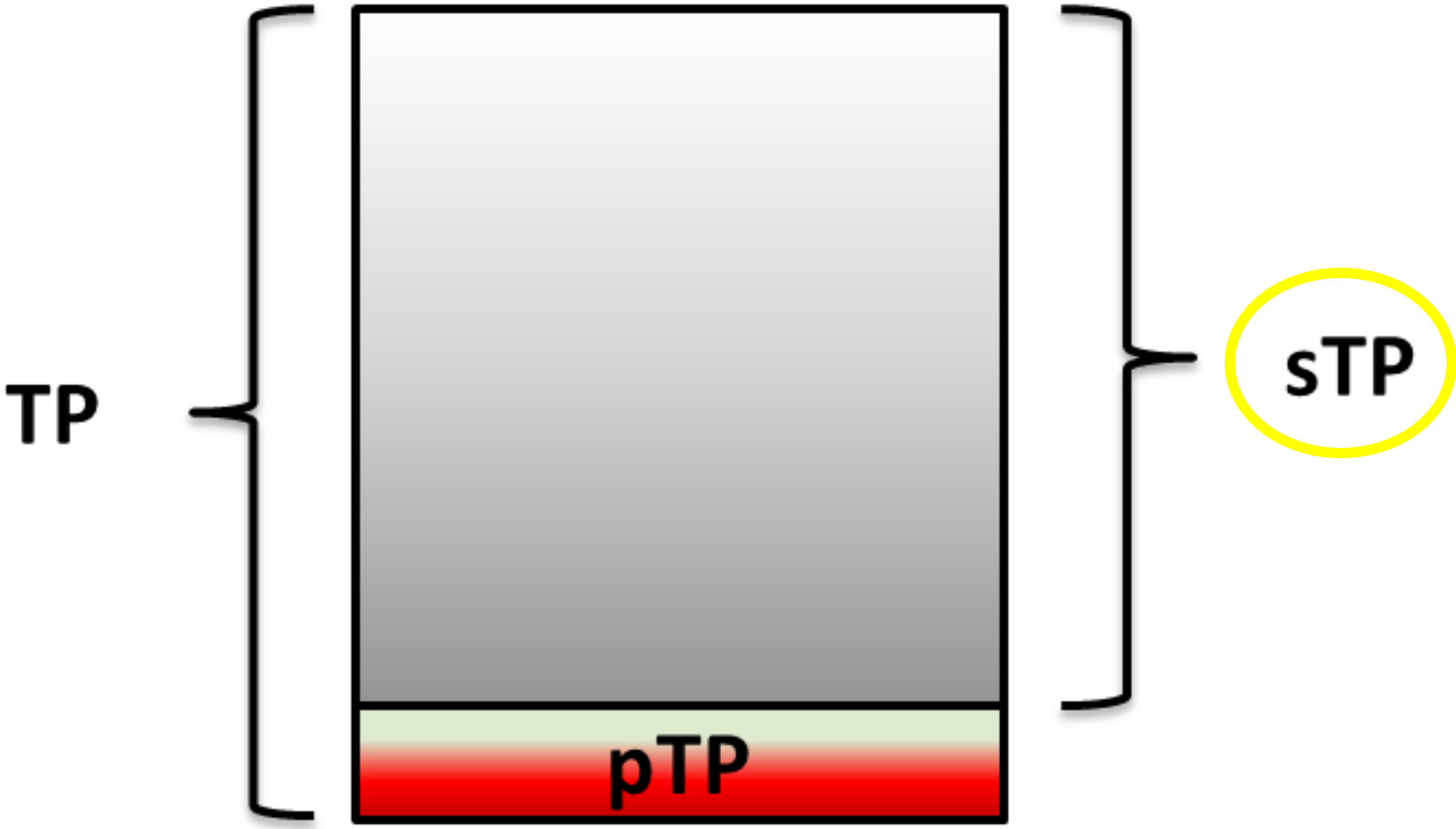
Persulfate Digestion

Direct Colorimetric Method



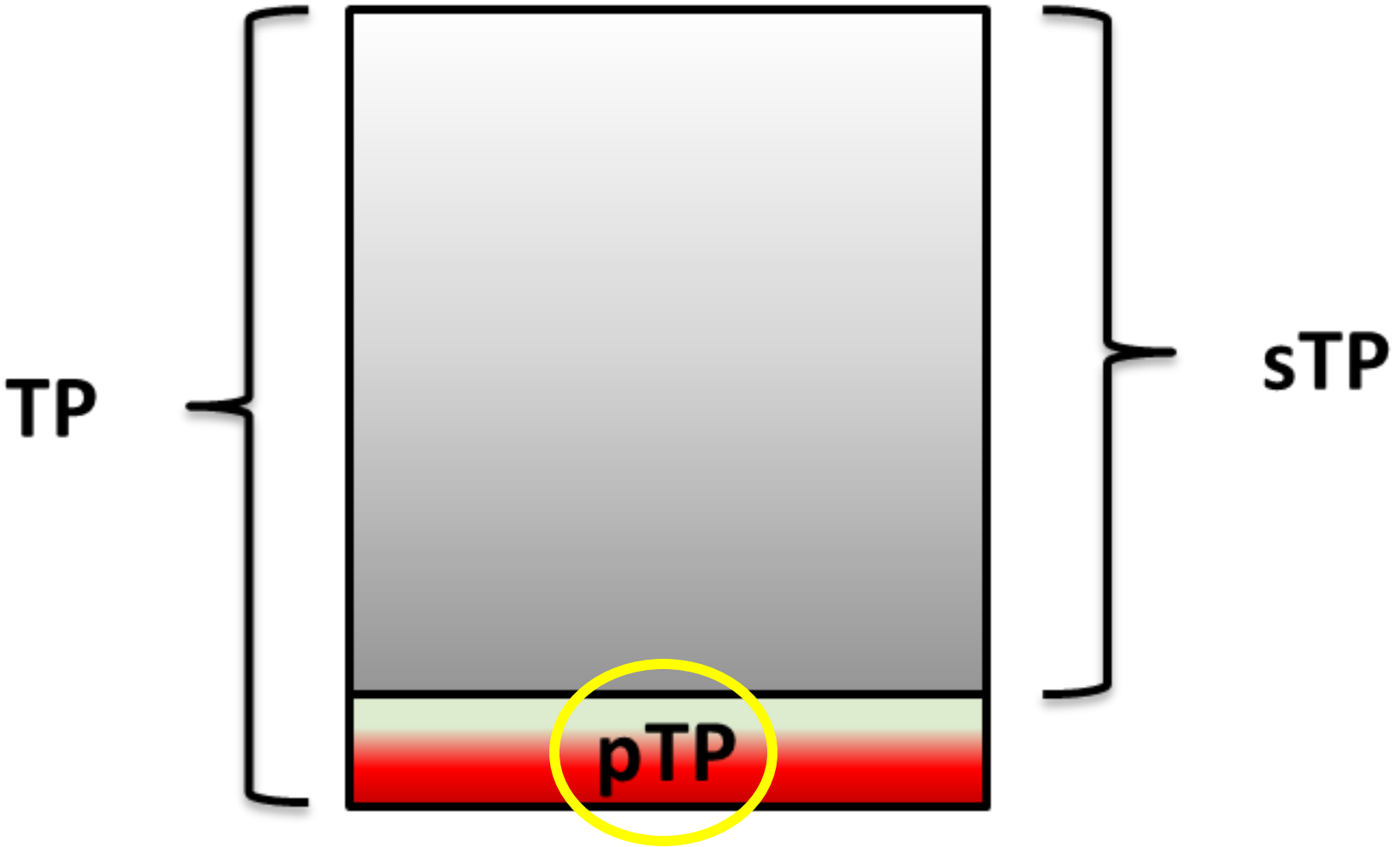
Total Soluble Phosphorus

Filter (0.45 Micron)/Persulfate Digestion
Direct Colorimetric Method



Total Particulate Phosphorus

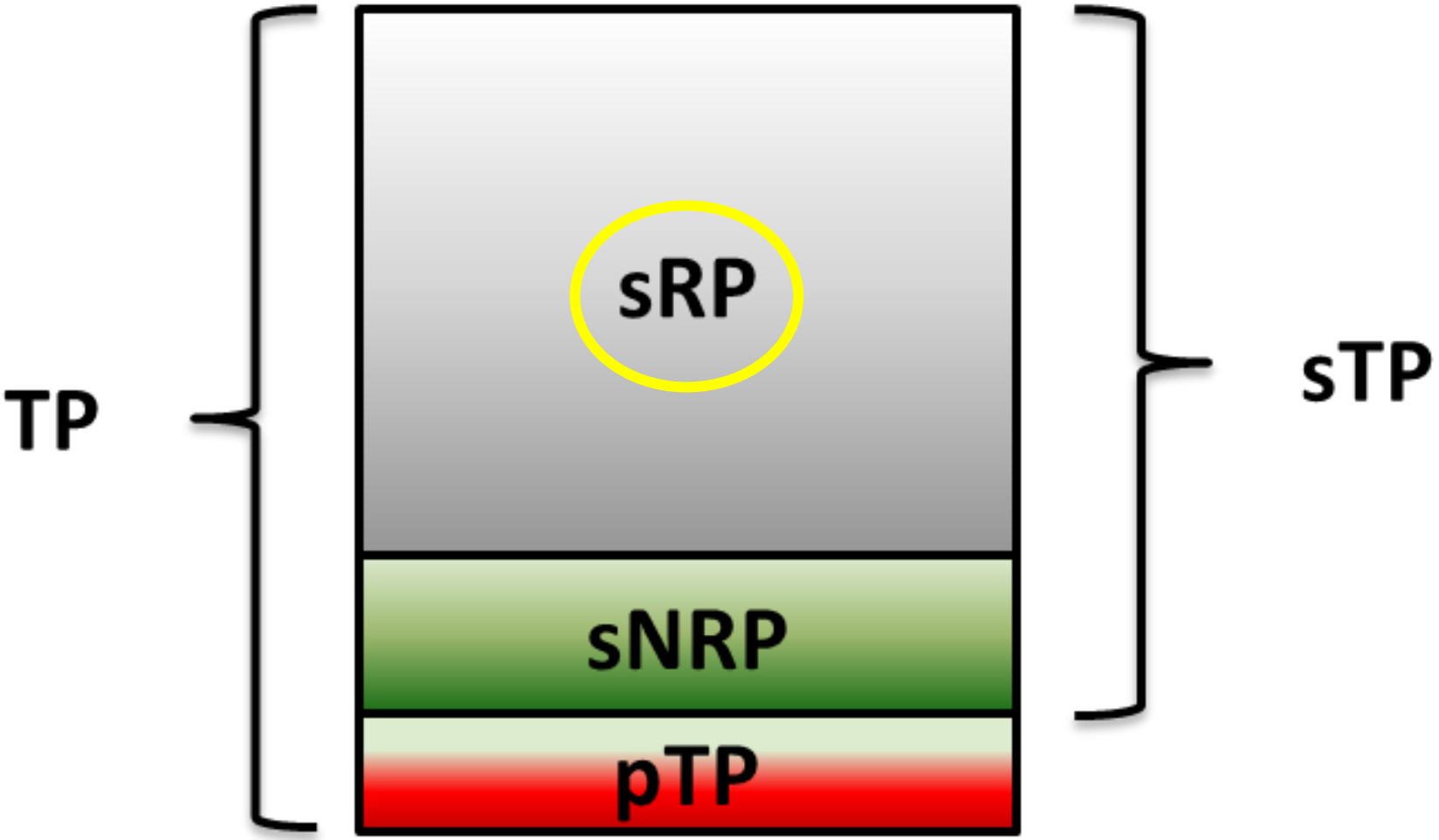
TP minus sTP



Soluble Reactive Phosphorus

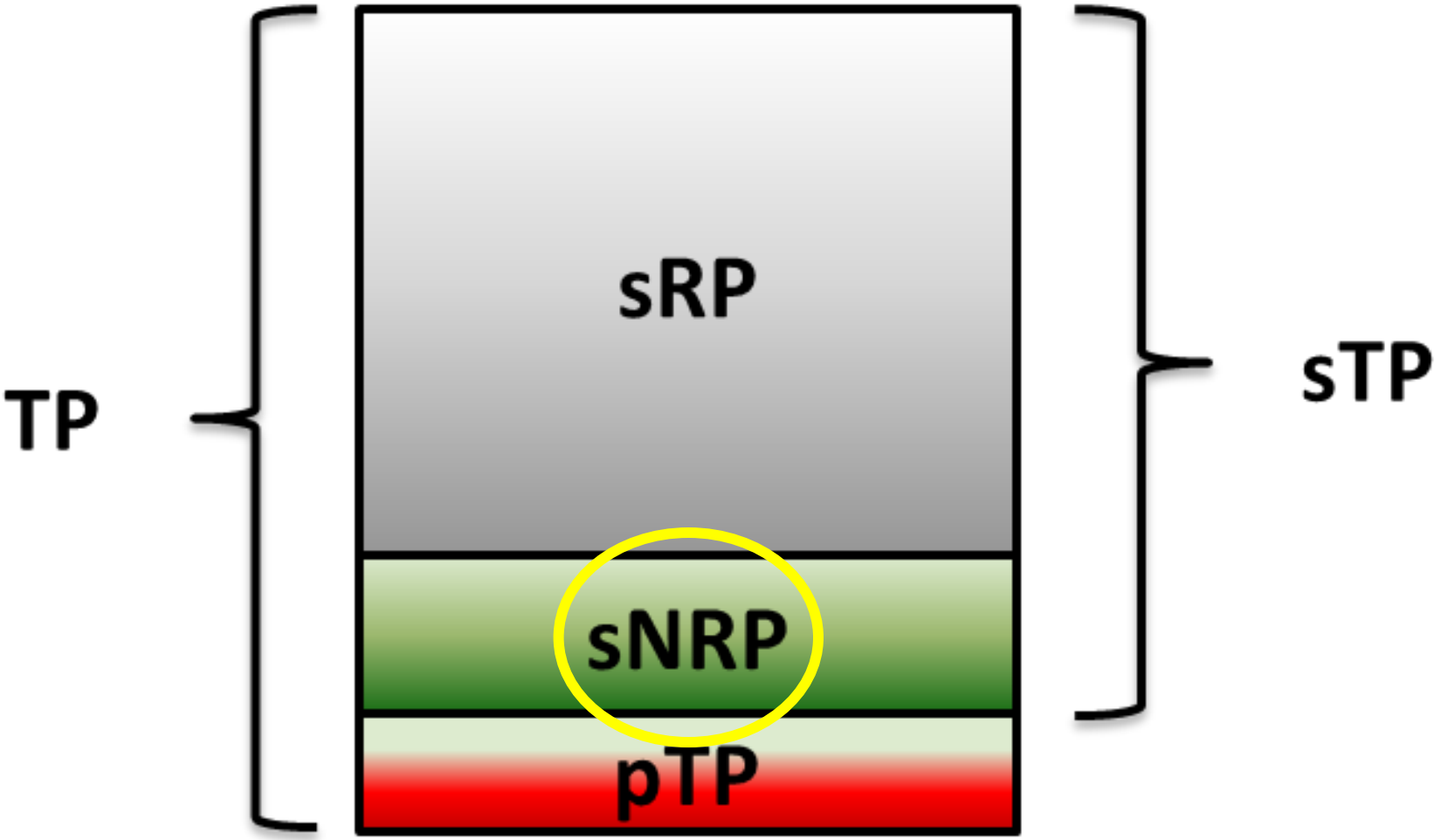
Filter (0.45 Micron)

Direct Colorimetric Method



Soluble Non-Reactive Phosphorus

sTP minus sRP



Additional Fractionation

- Gets a More Complete Picture
- Helps to UnderstaNd Treatability

Advanced – More Fractions of P

- Total Phosphorus can be divided into a total of 17 fractions or species
  - 5 of the fractions are directly from analyses tRP, tAHP, sTP, sAHP & sRP
  - The other 12 are calculated using the results of 6 different analyses

DOUBLE CALC

List of Fractions of P

Fraction of P	Abbrev.	Source
Total Phosphorus	TP	Analyze
Total Reactive Phosphorus	tRP	Analyze
Total Acid Hydrolysable Phosphorus	tAHP	Analyze
Total Non Reactive Phosphorus	tNRP	TP - tRP
Total Polymerized Phosphorus	tPoly	tAHP - tRP
Total Organic Phosphorus	tOP	TP - tAHP
Total Particulate Phosphorus	pTP	TP - sTP
Particulate Reactive Phosphorus	pRP	tRP - sRP
Particulate Organic Phosphorus	pOP	tOP - sOP
Particulate Non Reactive Phosphorus	pNRP	tNRP - sNRP
Particulate Polymerized Phosphorus	pPoly	tPoly - sPoly
Particulate Acid Hydrolysable Phosphorus	pAHP	tAHP - sAHP
Total Soluble Phosphorus	sTP	Analyze after 0.45 um filter
Soluble Acid Hydrolysable Phosphorus	sAHP	Analyze after 0.45 um filter
Soluble Reactive Phosphorus	sRP	Analyze after 0.45 um filter
Soluble Organic Phosphorus	sOP	sTP - sAHP
Soluble Non Reactive Phosphorus	sNRP	sTP - sRP
Soluble Polymerized Phosphorus	sPoly	sAHP - sRP

BeWare !!!

TWO DIFFERENT PATHWAYS -----

- As part of analyzing for fractions of P:
- There are two totally different procedures/pathways to arrive at the various analyzed fractions of P
  - Pathway (1) **TP** - Persulfate digestion followed by colorimetry
  - Pathway (2) **Acid hydrolyzable** - Acid hydrolysis followed by digestion and then colorimetry.

BeWare !!!

TWO DIFFERENT PATHWAYS -----

- These two different procedures may result in an issue where all of the analyzed and calculated fractions of P do not add up EXACTLY the TOTAL PHOSPHORUS value.
- See following 2 slides

From Hach Method for ACID HYDROLYZABLE PHOSPHORUS (AHP)

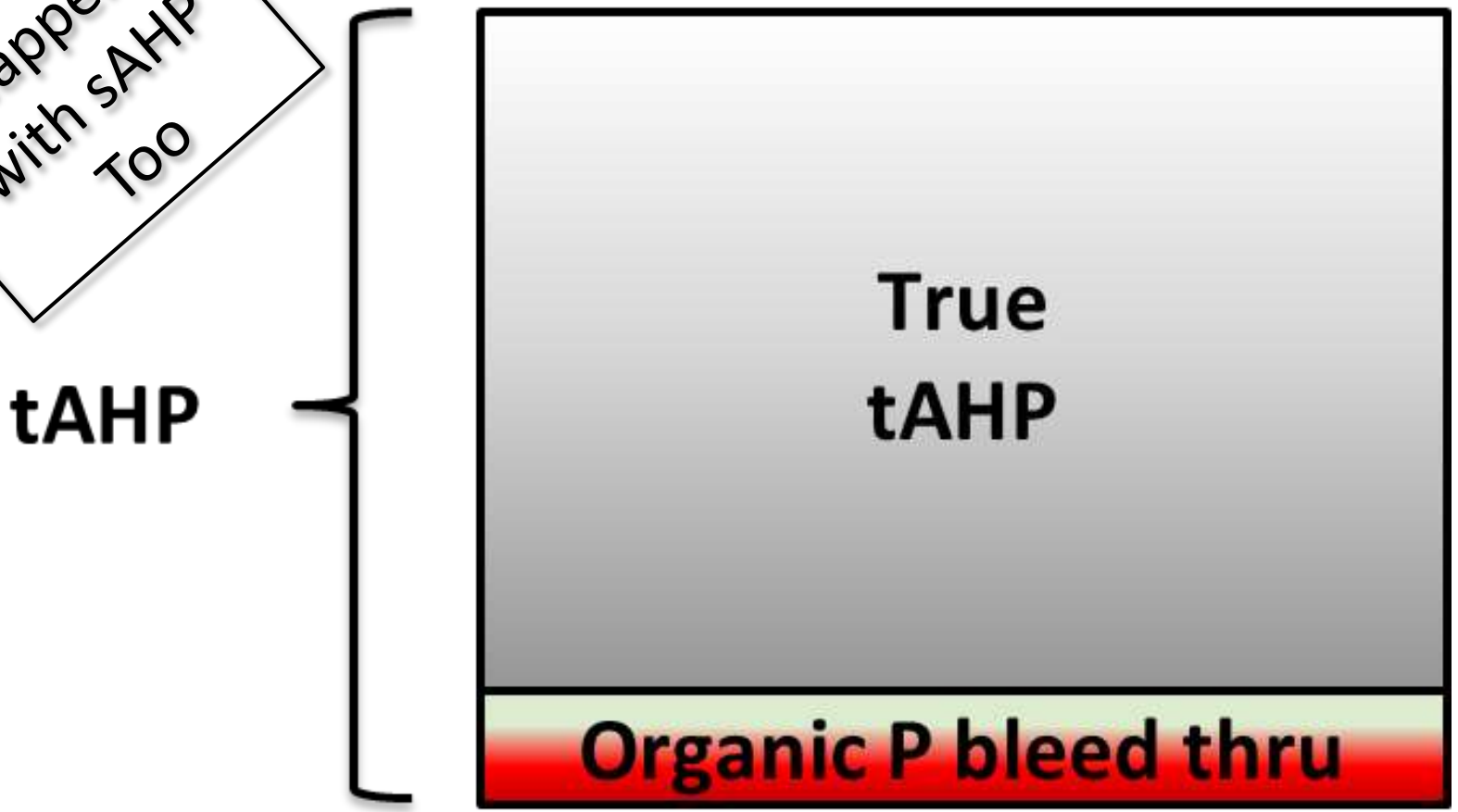
"The procedure uses acid and heat to hydrolyze the sample. Organic phosphates are not converted to orthophosphate by this process, ***but a very small fraction may be unavoidably included in the result.***"

Troubles with Analysis

- **STEP 1** - AHP analysis uses **ACID** & **HEAT** to convert condensed (polymerized) Phosphorus to **orthophosphate**
- NOTE --- Organic P does convert to orthophosphate in STEP 1
- **STEP 2** – Once condensed P is converted to ortho-P a simple color based orthophosphate test is used to measure P levels
- **BUT** - ***small amount of ORGANIC P may in fact bleed through and be converted to orthophosphate in STEP 1***
- May shows up as part of the tAHP & sAHP results

Possible Organic P Bleed Thru

Could Happen with sAHP Too



Be Aware

- Filter samples right away after collecting so any P within solids don’t end up dissolving into the liquid phase
- Run Soluble & Total Reactive Phosphorus analyses right away

How do

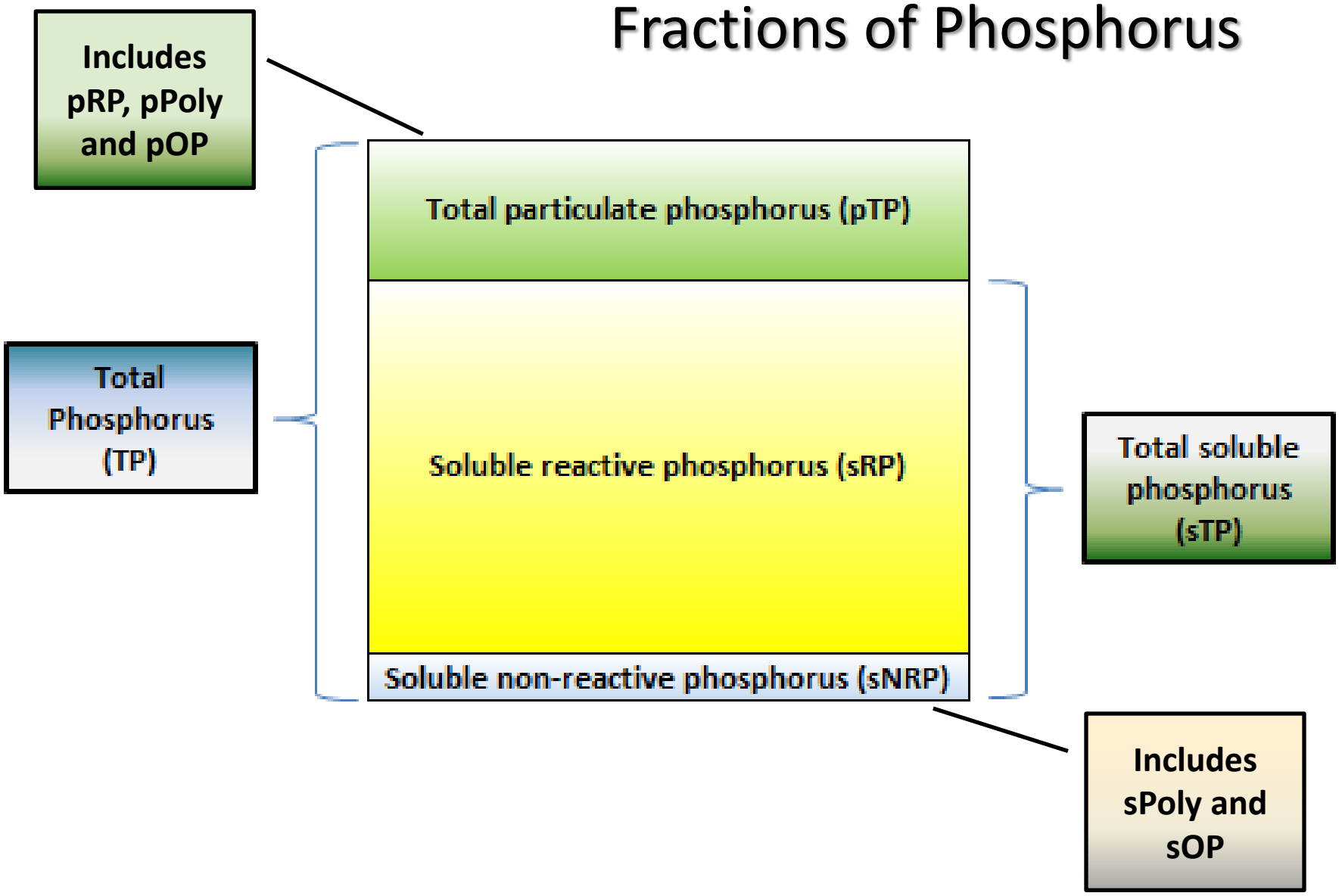
get the More Complex

FRACTIONS OF P ???

NOW:

Here's ALL the Fractions

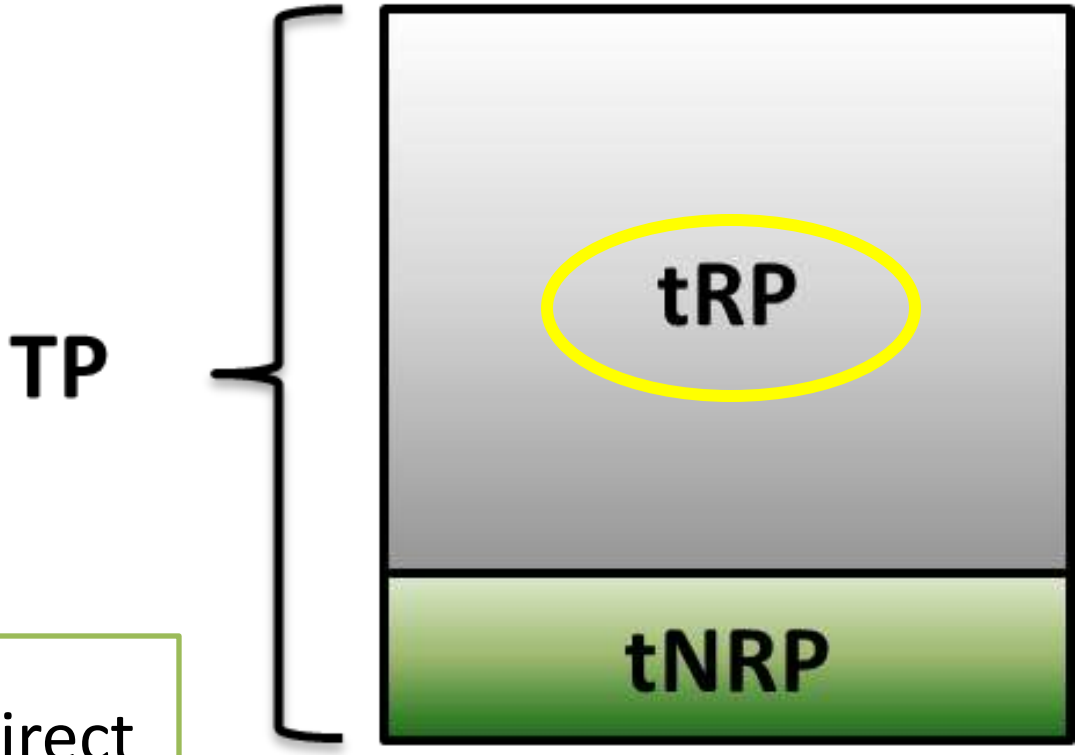
Summary of (p, Poly & s) Fractions of Phosphorus



Fractions of TOTAL(t) P

Total Reactive Phosphorus (tRP)

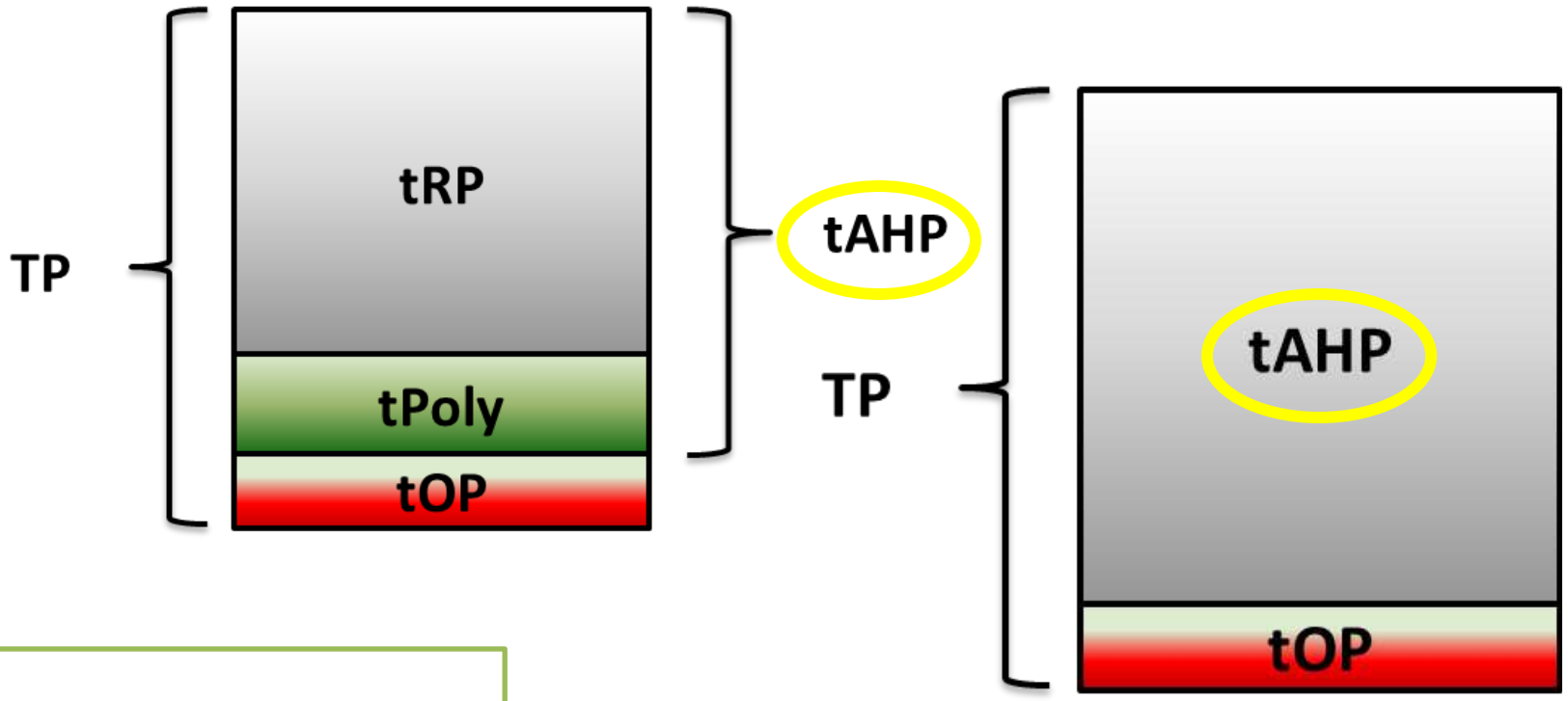
Direct Analysis



tRP is direct analysis

Total Acid Hydrolysable Phosphorus (tAHP)

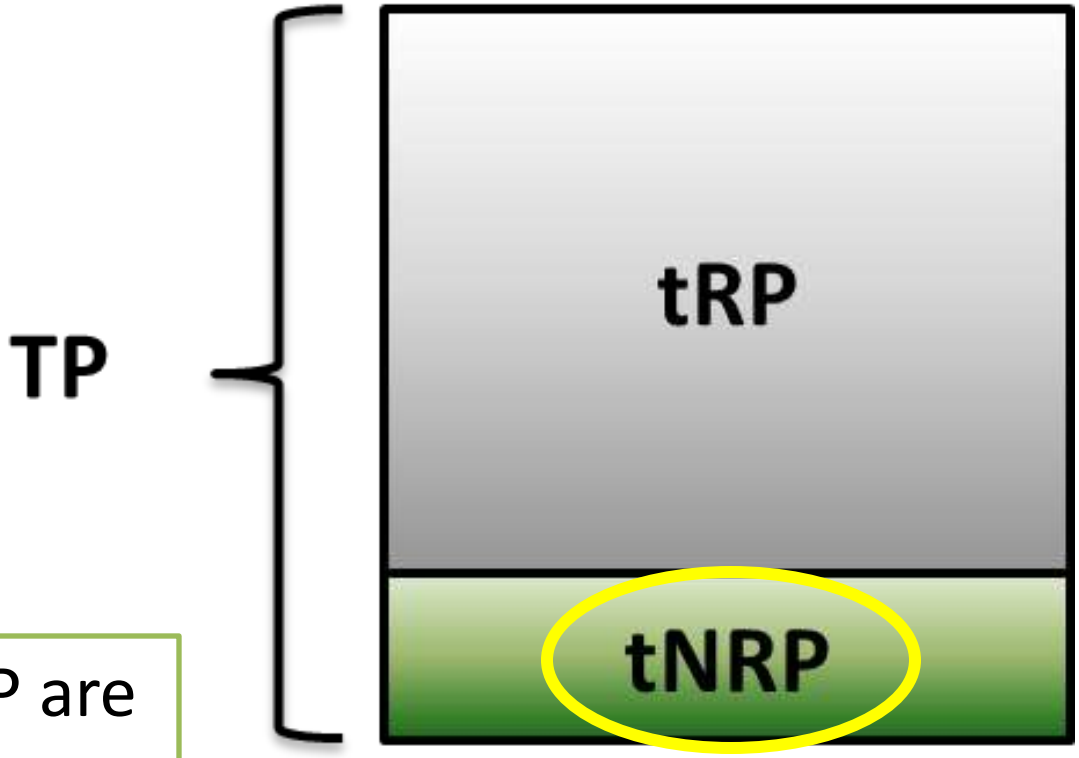
Direct Analysis



tAHP is direct analysis

Total Non-Reactive Phosphorus (tNRP)

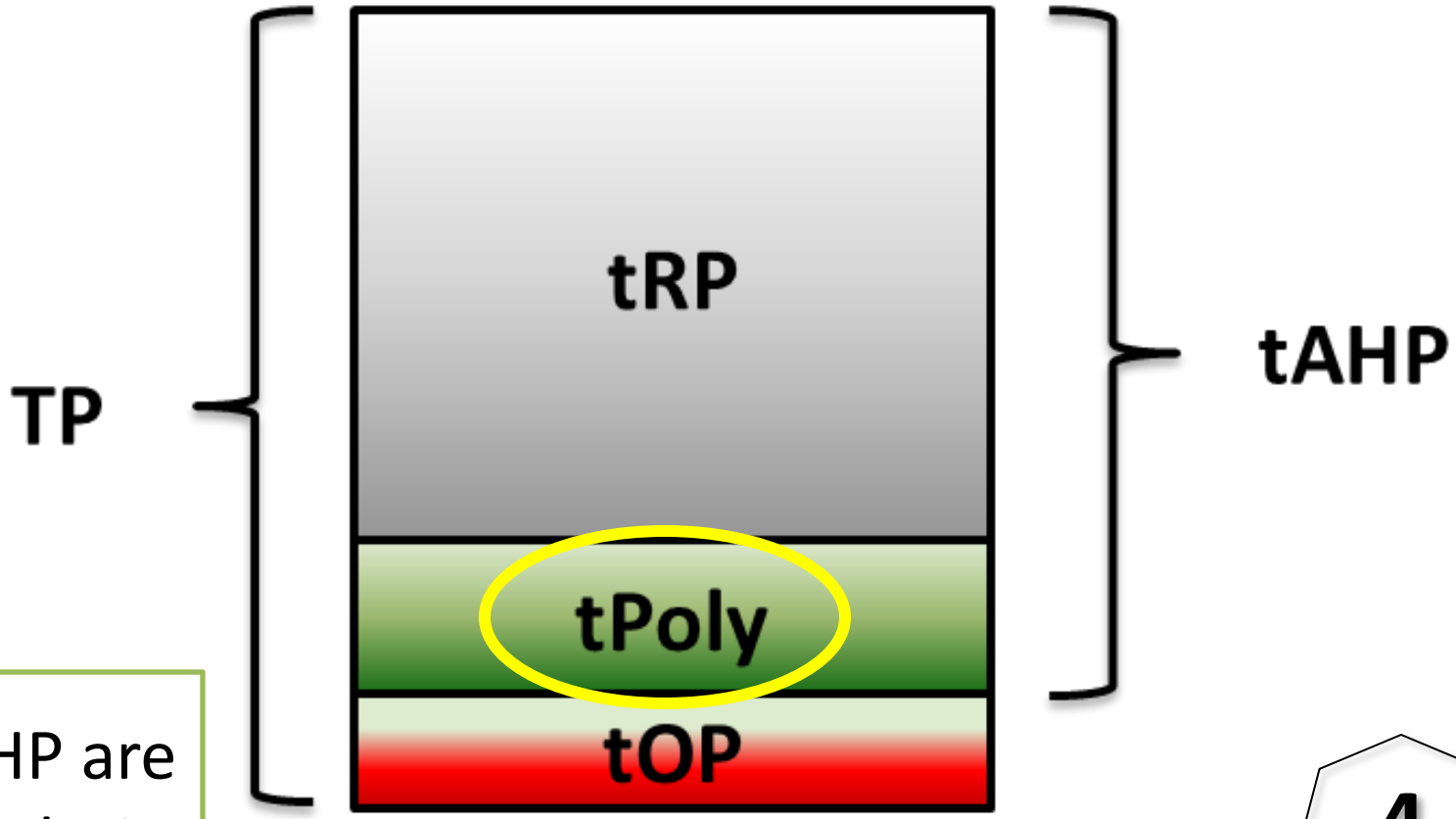
TP - tRP



TP & tRP are direct analysis

Total Polymerized Phosphorus (tPoly)

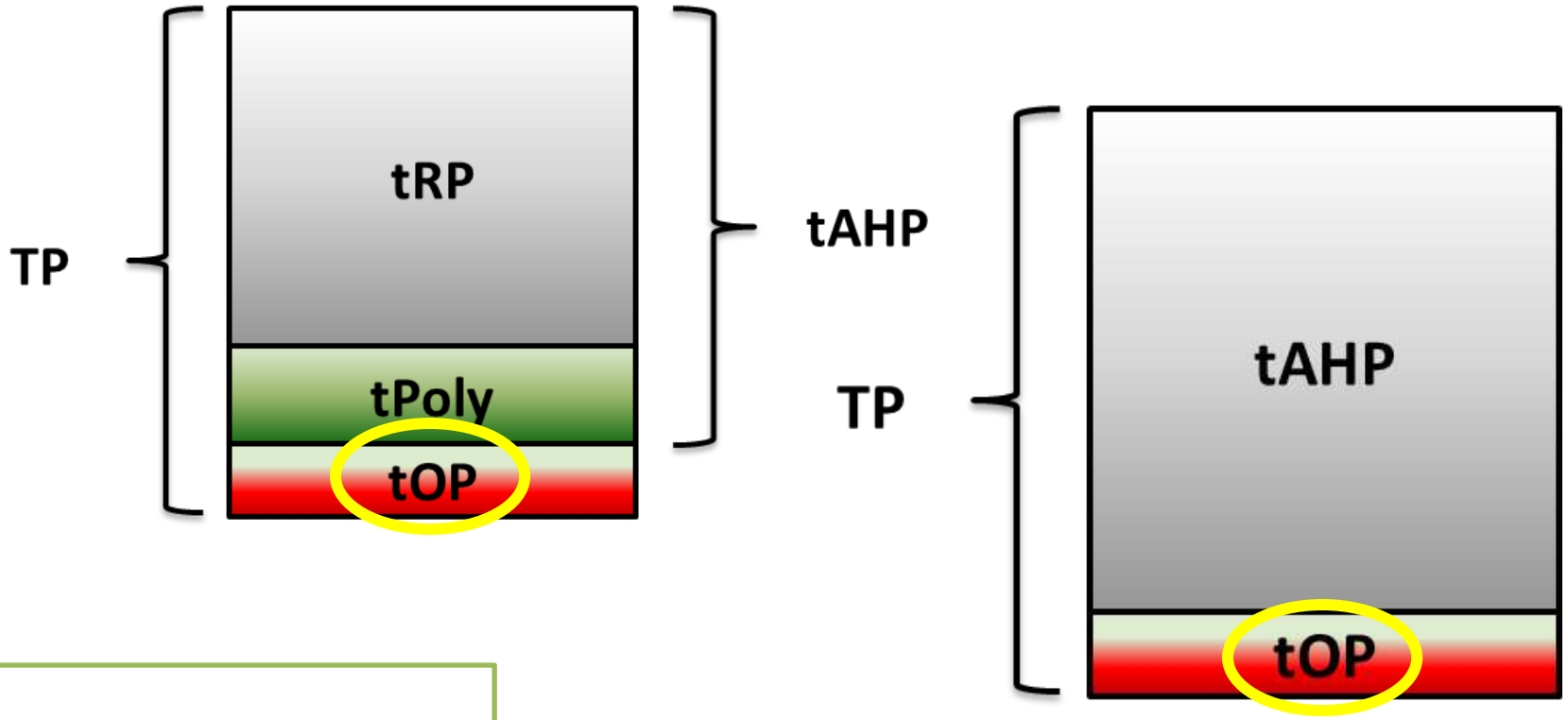
tAHP - tRP



tRP & tAHP are direct analysis

Total Organic Phosphorus (tOP)

TP - tAHP

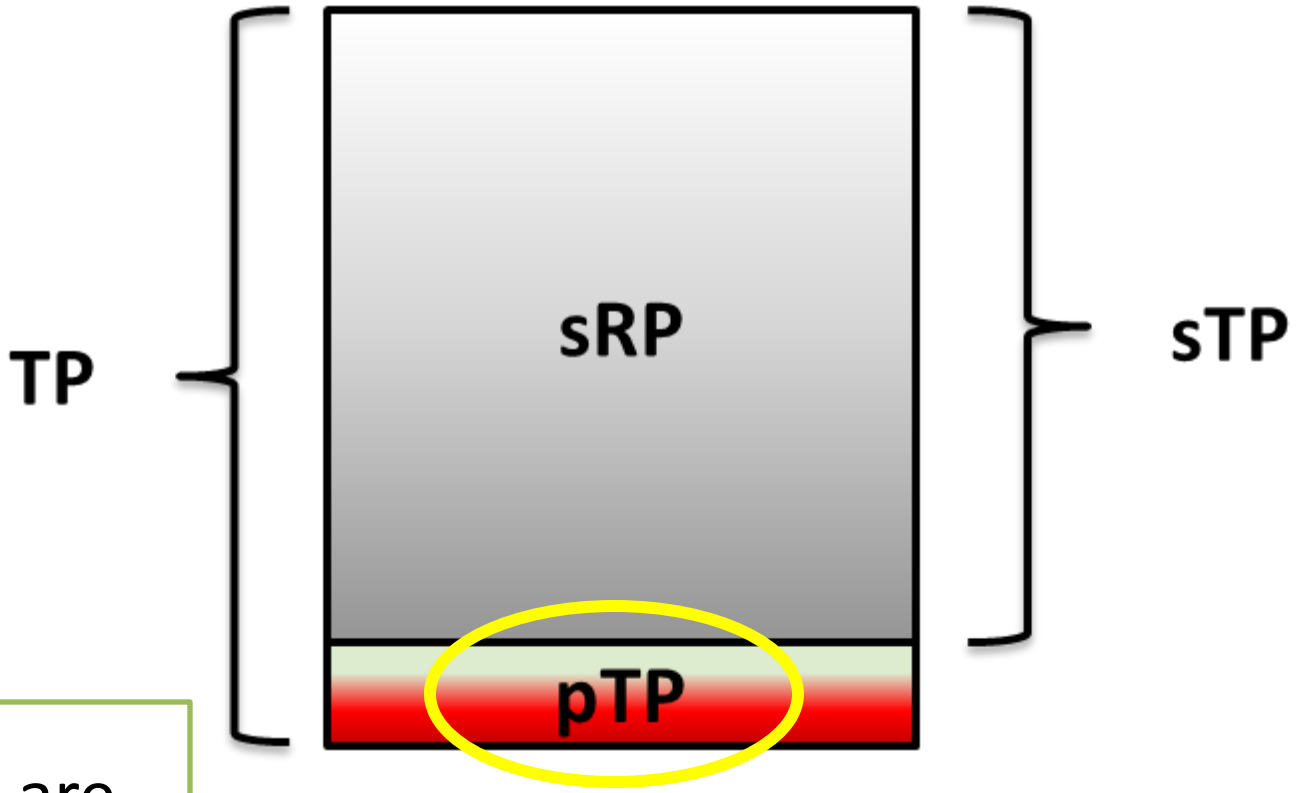


TP & tAHP are direct analysis

Fractions of Particulate (p) P

Total Particulate Phosphorus (pTP)

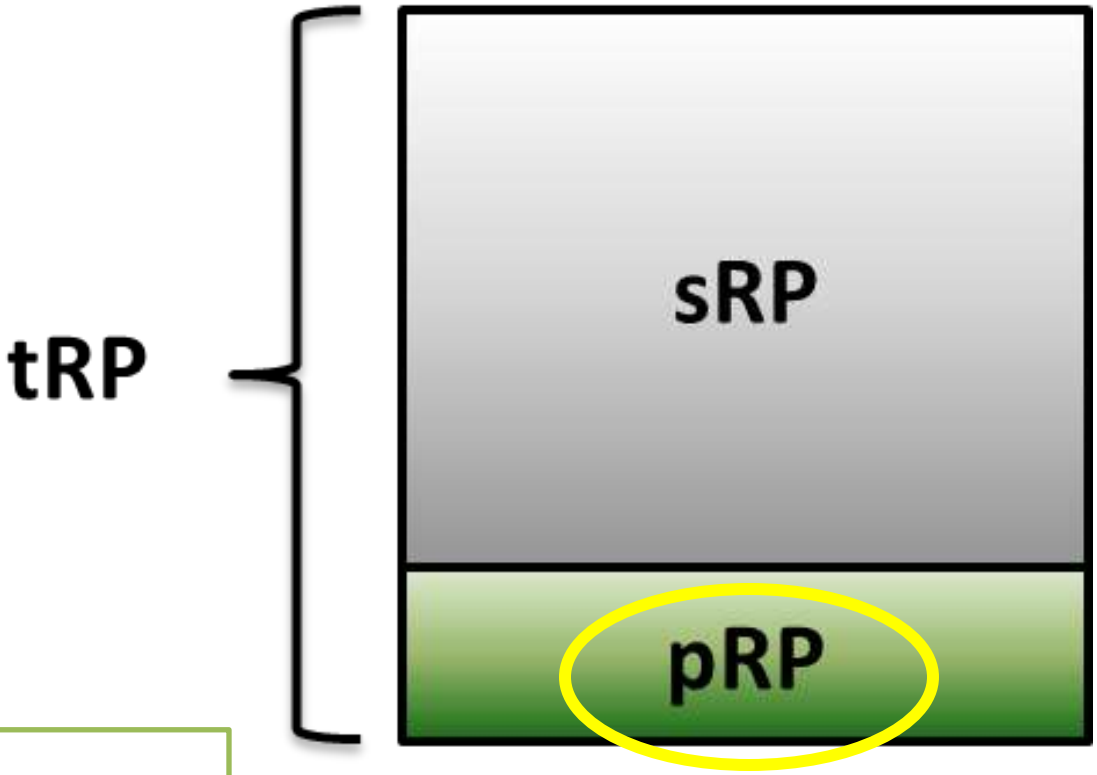
TP - sTP



TP & sTP are direct analysis

Particulate Reactive Phosphorus (pRP)

tRP - sRP

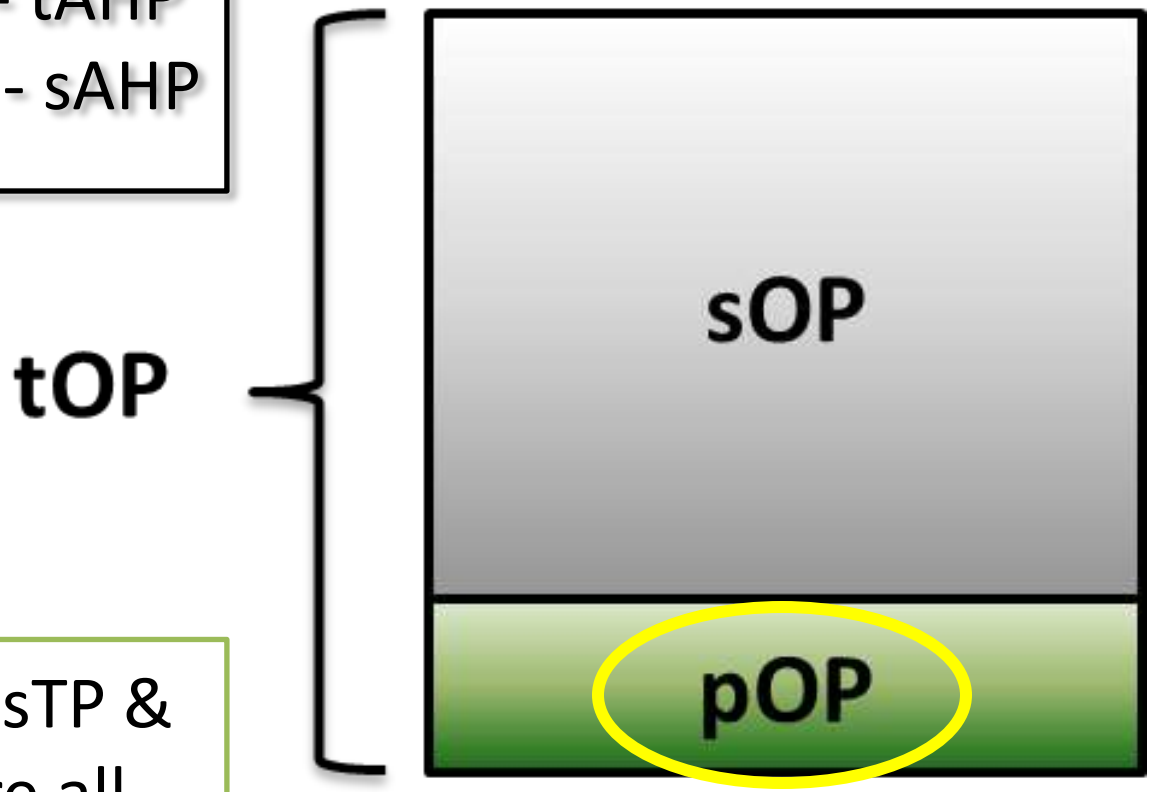


tRP & sRP are direct analysis

Particulate Organic Phosphorus (pOP)

tOP - sOP

tOP = TP - tAHP
sOP = sTP - sAHP

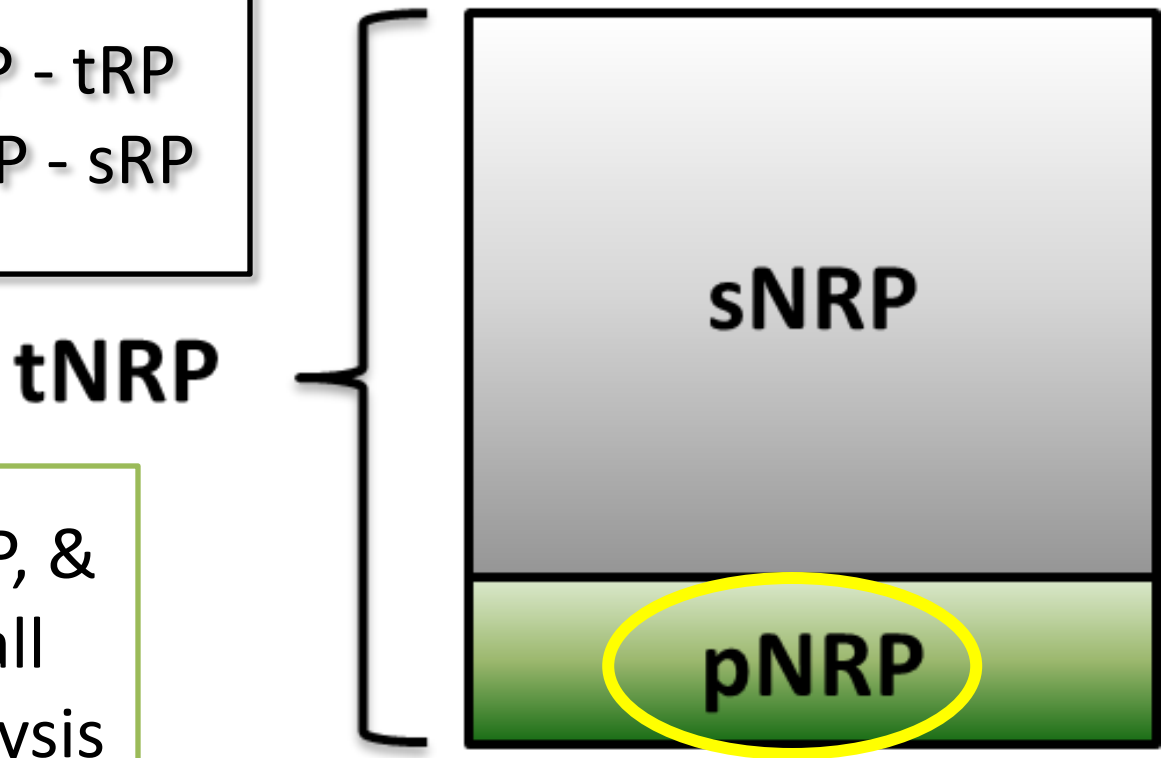


TP, tAHP, sTP & sAHP are all direct analysis

Particulate Non-Reactive Phosphorus (pNRP)

tNRP - sNRP

tNRP = TP - tRP
sNRP = sTP - sRP

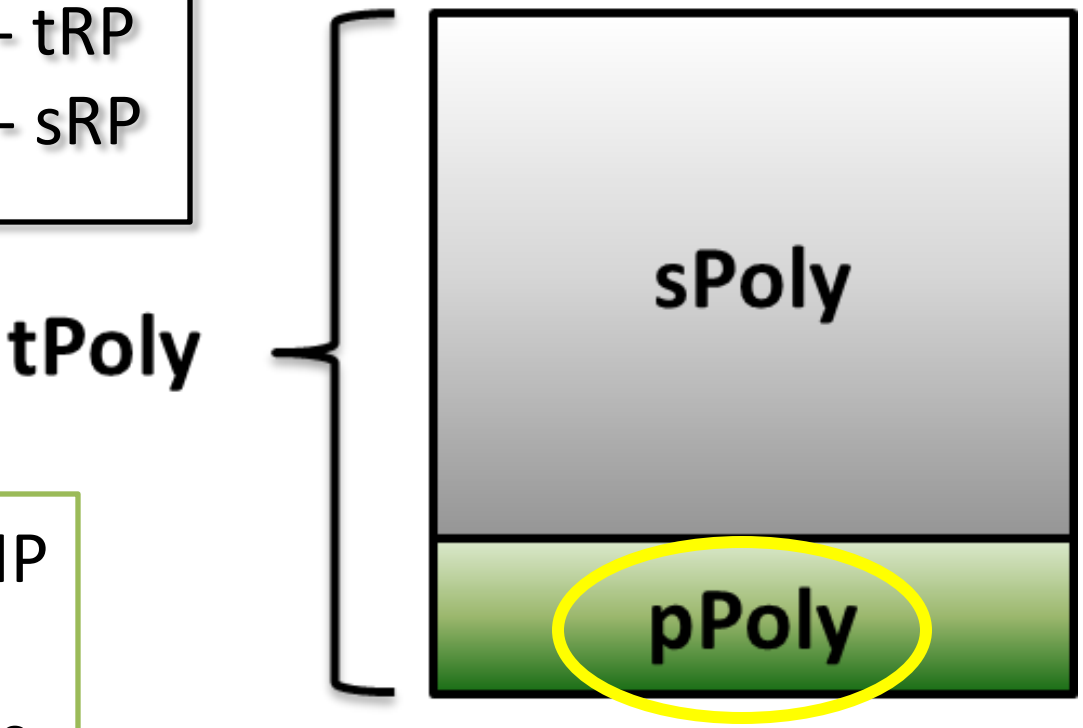


TP, tRP, sTP, & sRP are all direct analysis

Particulate Polymerized Phosphorus (pPoly)

tPoly - sPoly

tPoly = tAHP - tRP
sPoly = sAHP - sRP

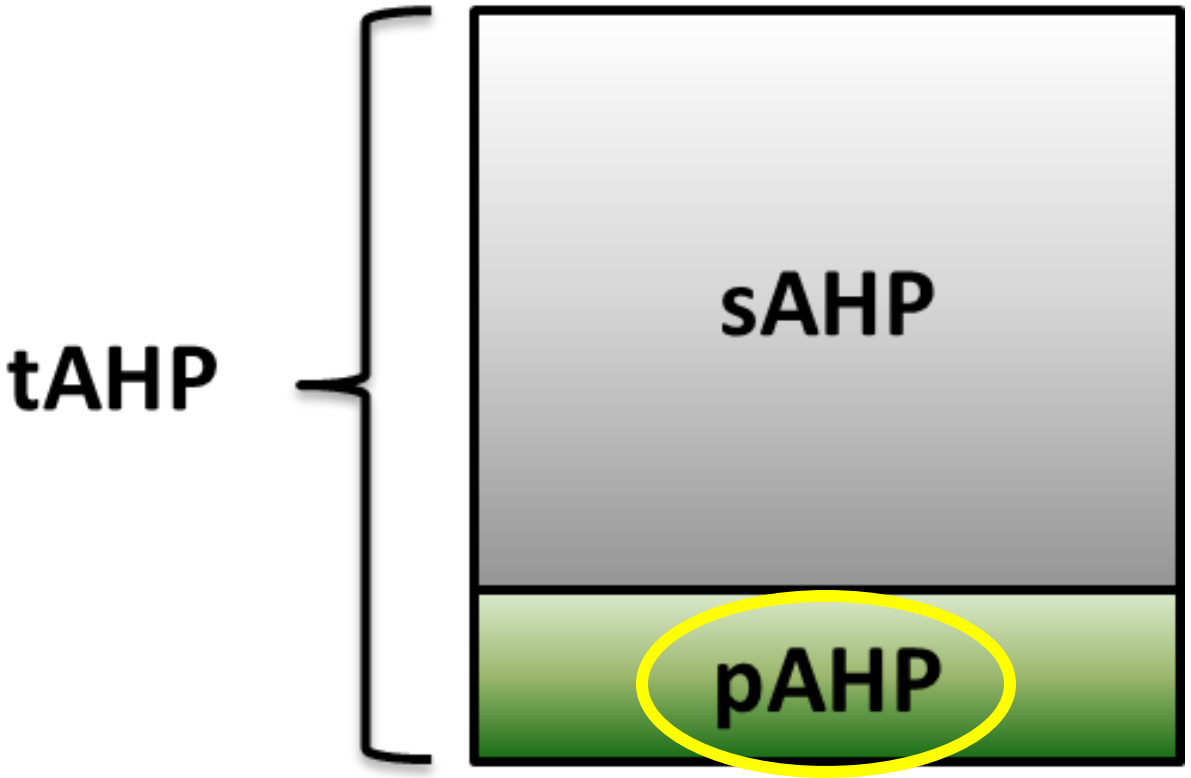


tAHP, tRP, sAHP & sRP are all direct analysis

tAHP & sAHP are direct analysis

pAHP

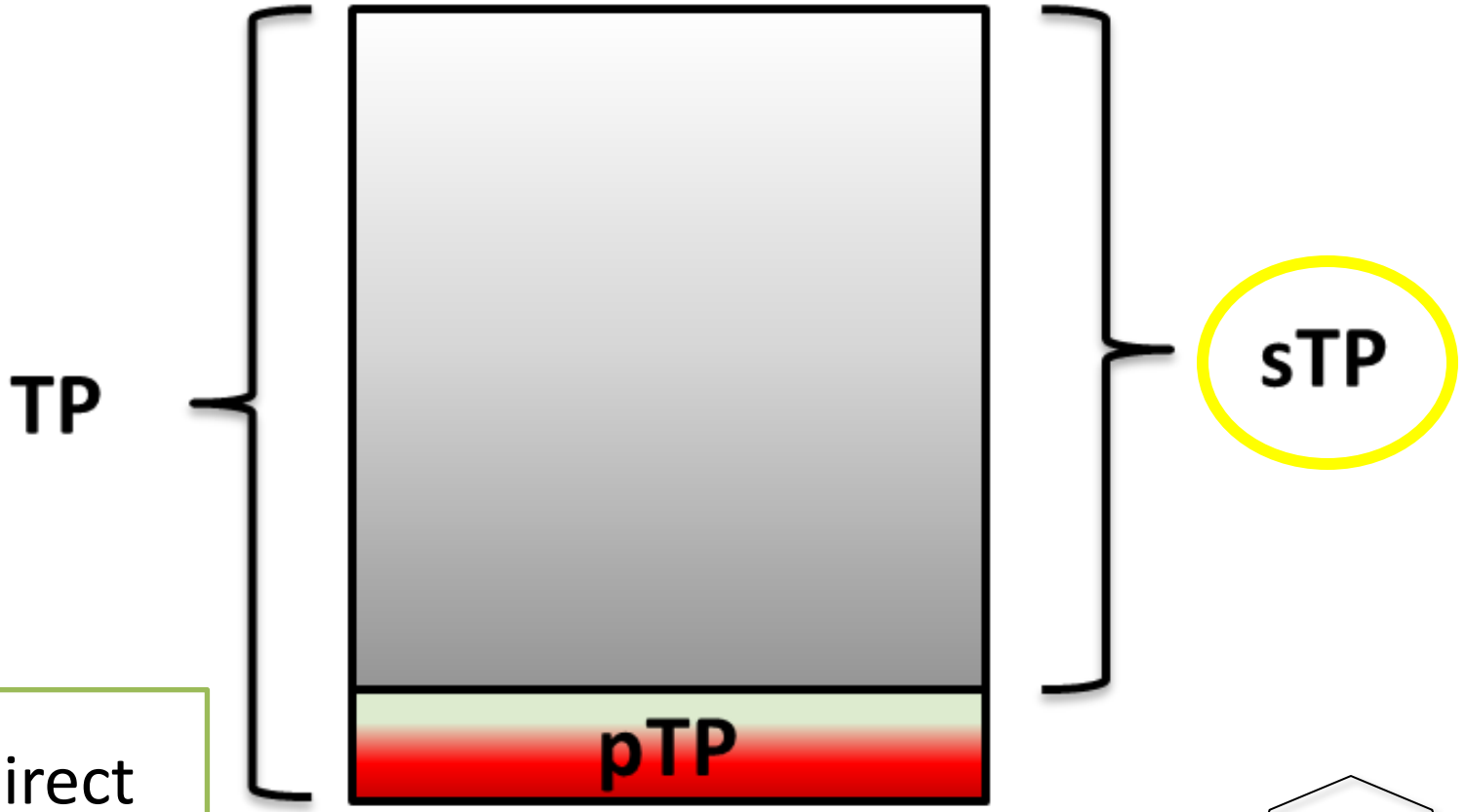
tAHP - sAHP



Fractions of SOLUBLE (s) P

Total Soluble Phosphorus (sTP)

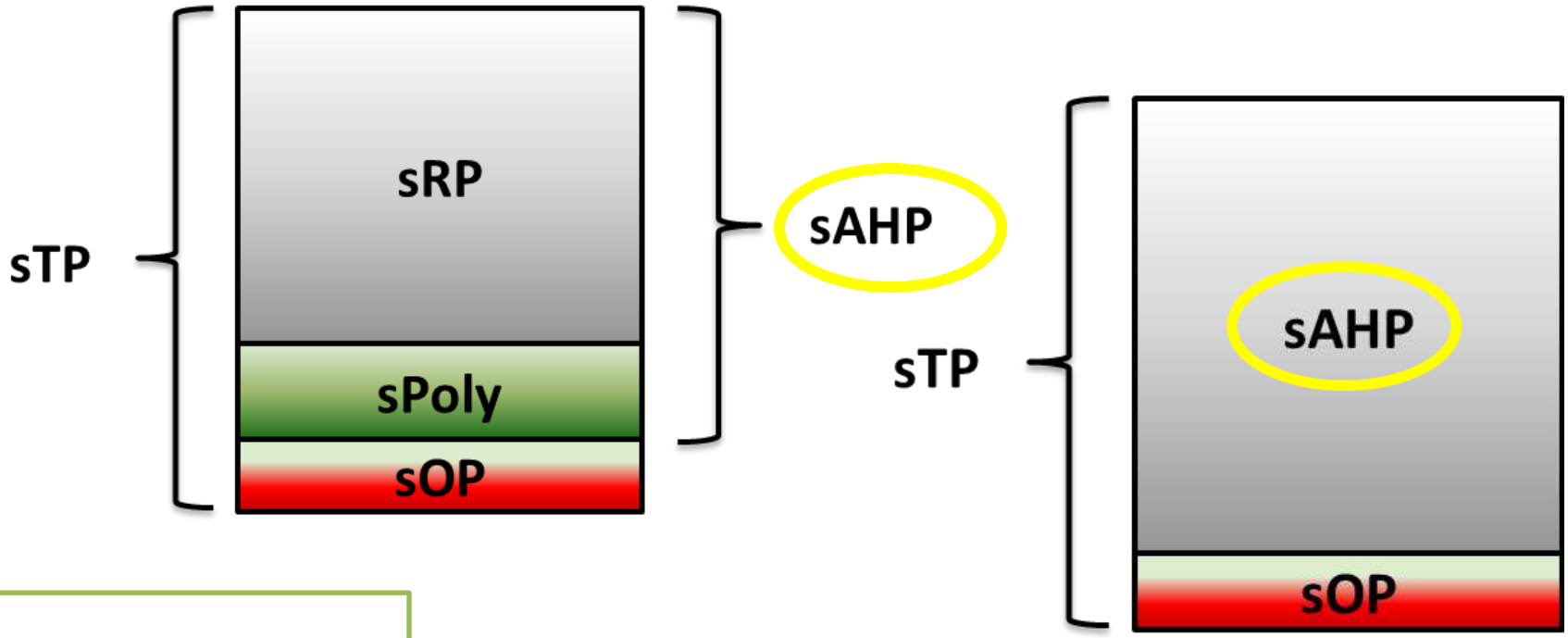
Direct Analysis



sTP is a direct analysis

Soluble Acid Hydrolysable Phosphorus (sAHP)

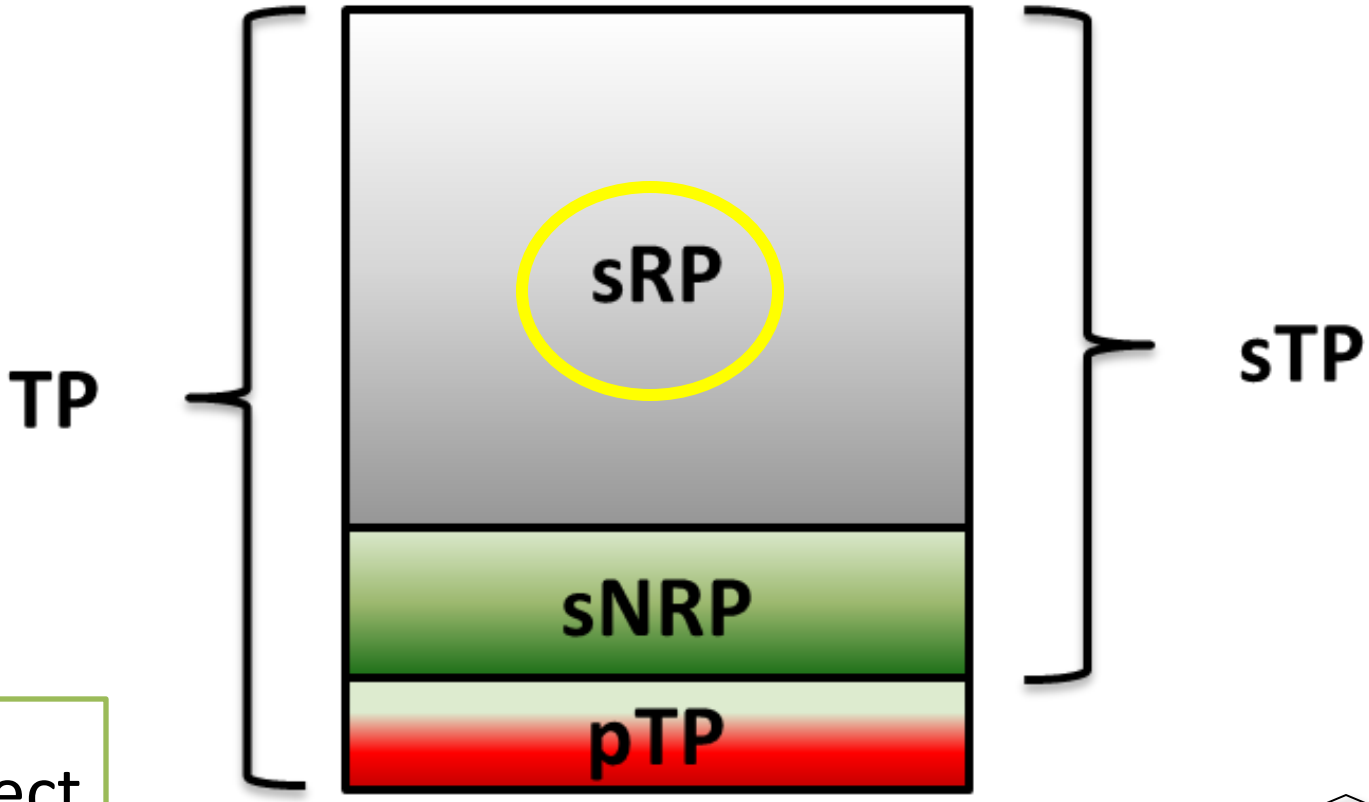
Direct Analysis



sAHP is a direct analysis

Soluble Reactive Phosphorus (sRP)

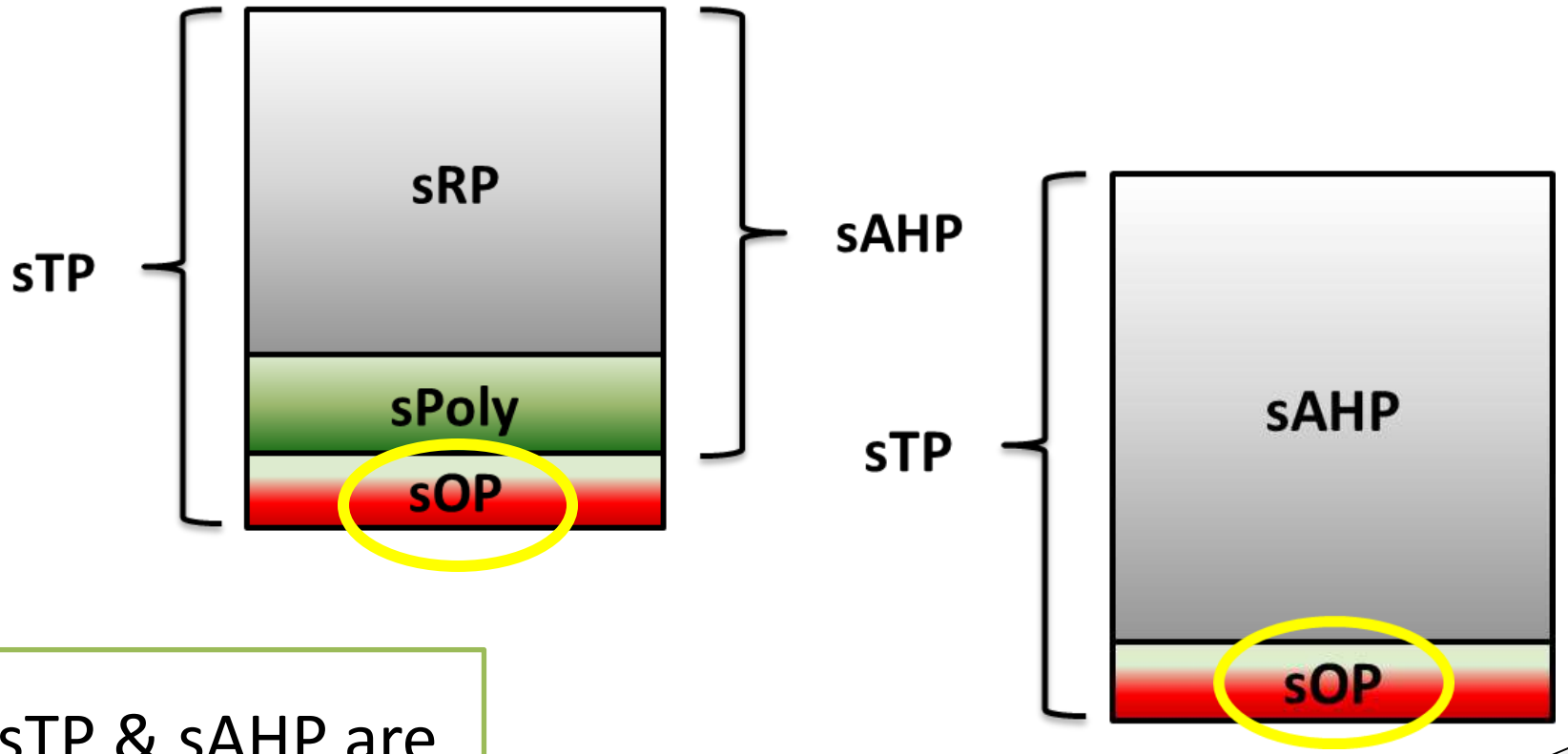
Direct Analysis



sRP is a direct analysis

Soluble Organic Phosphorus (sOP)

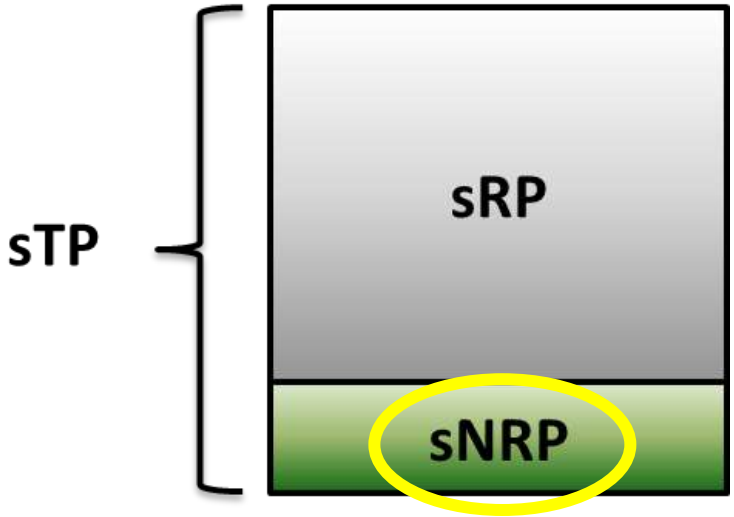
sTP - sAHP

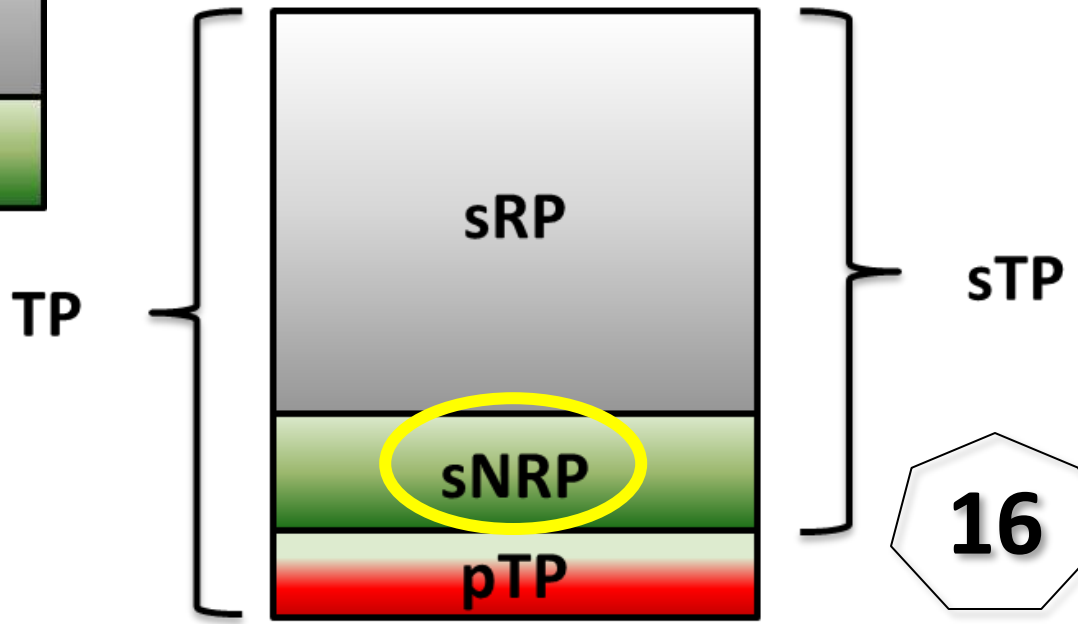


sTP & sAHP are direct analysis

Soluble Non-Reactive Phosphorus(sNRP)

sTP - sRP

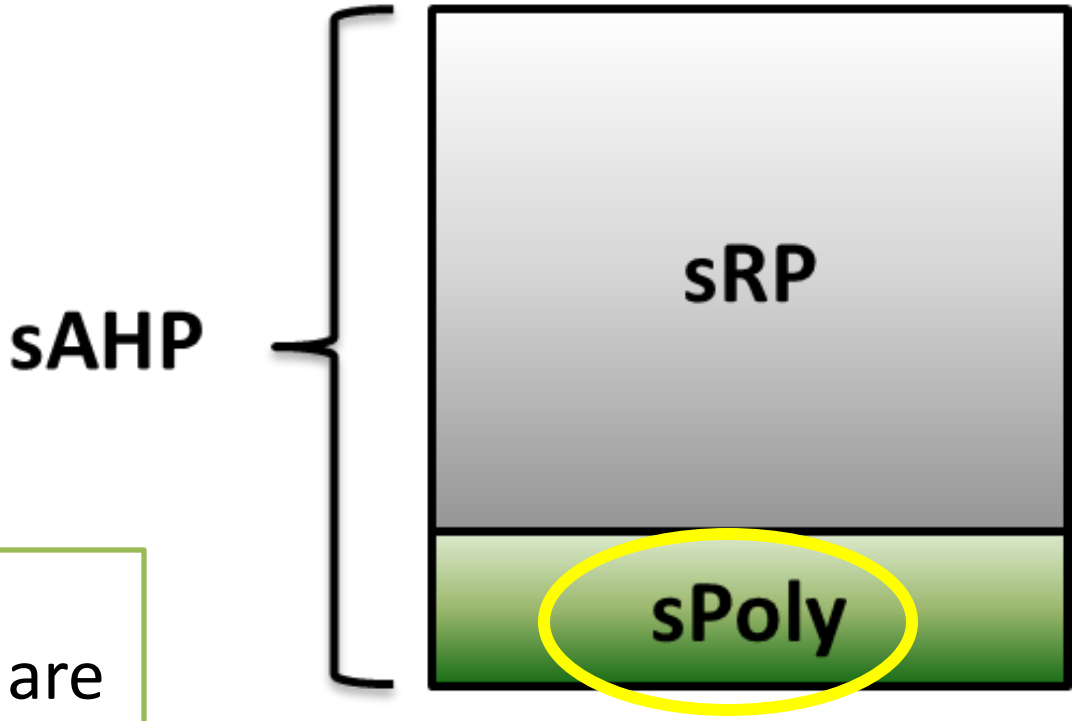




sTP & sRP are direct analysis

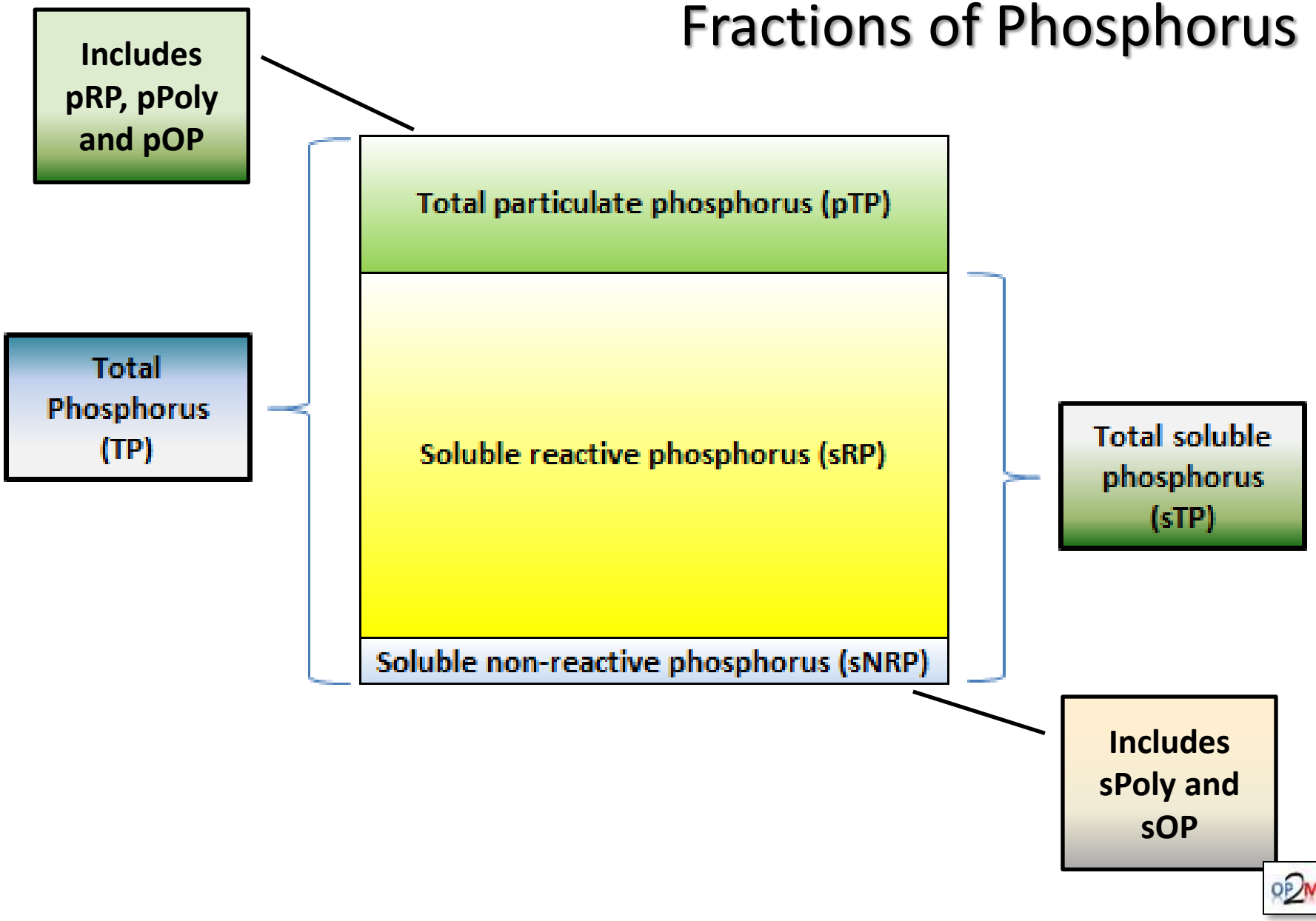
Soluble Polymerized Phosphorus(sPoly)

sAHP - sRP



sRP & sAHP are direct analysis

Summary of (p, Poly & s) Fractions of Phosphorus



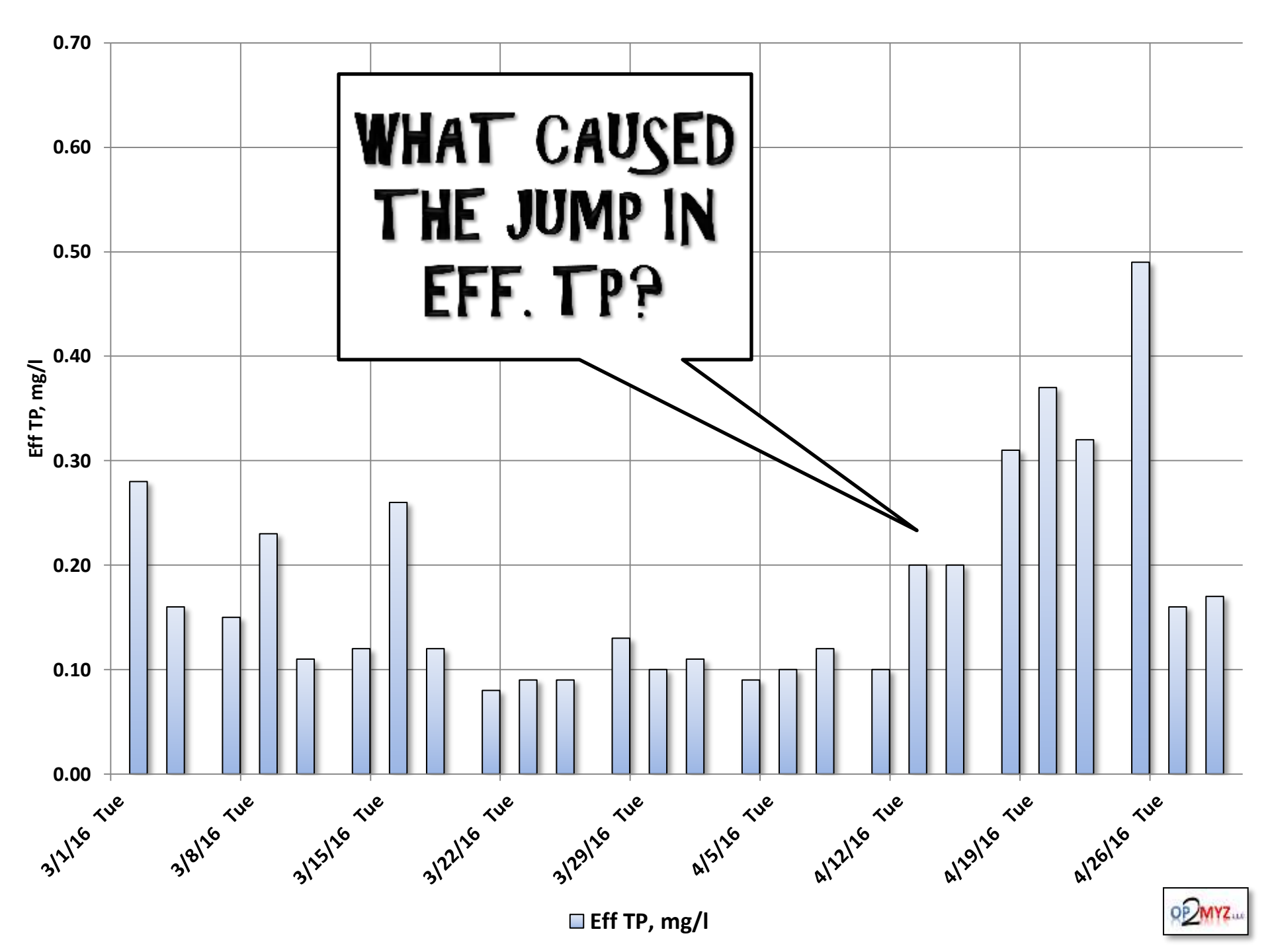
Why Bother

with the

FRACTIONS OF P ???

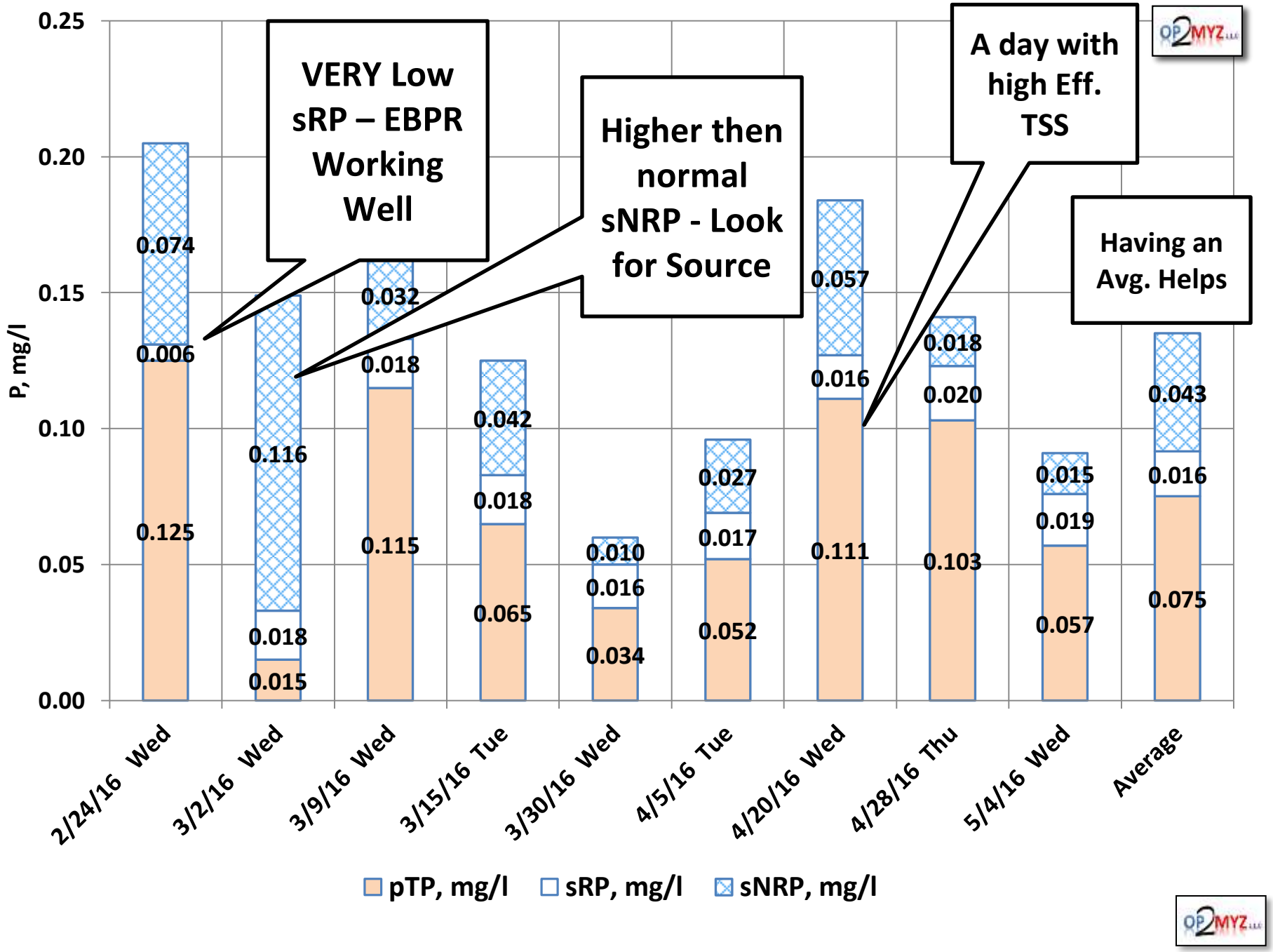
Why Fractionalize P ?

- We want to understand how to approach phosphorus treatment
- Best way is to understand each fraction and its make up
- Once known, treatment options become more clear


WHAT CAUSED THE JUMP IN EFF. TP?
Eff TP, mg/l
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
3/1/16 Tue
3/8/16 Tue
3/15/16 Tue
3/22/16 Tue
3/29/16 Tue
4/5/16 Tue
4/12/16 Tue
4/19/16 Tue
4/26/16 Tue
Eff TP, mg/l

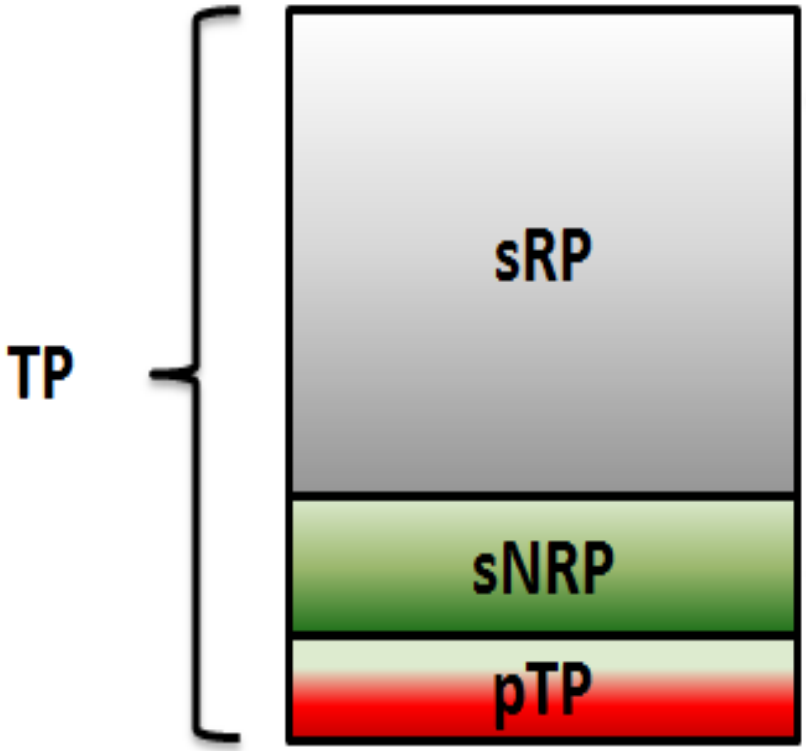
WHAT CAUSED THE JUMP IN EFF. TP?

- Analyze → basic fractions then;
  - You  what makes up TP
  - Adjust appropriate treatment to reduce species
  - Reduce source
  - Work better with engineers to design a fitting and efficient processes for P removal


VERY Low sRP – EBPR Working Well
Higher then normal sNRP - Look for Source
A day with high Eff. TSS
Having an Avg. Helps
P, mg/l
0.25
0.20
0.15
0.10
0.05
0.00
0.074
0.006
0.125
0.116
0.018
0.015
0.032
0.018
0.115
0.042
0.018
0.065
0.010
0.016
0.034
0.027
0.017
0.052
0.057
0.016
0.111
0.018
0.020
0.103
0.015
0.019
0.057
0.043
0.016
0.075
2/24/16 Wed
3/2/16 Wed
3/9/16 Wed
3/15/16 Tue
3/30/16 Wed
4/5/16 Tue
4/20/16 Wed
4/28/16 Thu
5/4/16 Wed
Average
pTP, mg/l
sRP, mg/l
sNRP, mg/l

3 Main Basic Fractions of P and Their General Treatment Pathway

- Soluble Reactive Phosphorus (**sRP**)
  - Chemical & BPR
- Soluble Non-Reactive Phosphorus (**sNRP**) which does not react well
  - Most difficult to remove
- Total Particulate (**pTP**) which is the phosphorus in the solids
  - Enhanced Settling & Filtration



Soluble Reactive Phosphorus (**sRP**)
Treatment: Chemical & EBPR

Soluble Non-Reactive Phosphorus (**sNRP**)
Treatment: Limited removal with Chemical & EBPR - Does NOT React Well, Most Difficult to Remove

Total Particulate Phosphorus (**pTP**)
Treatment: **Enhanced Settling & Filtration**

Example of Reactive vs. Non-Reactive & Soluble NRP vs. Particulate NRP

Removing the Fractions

Fraction	Removal Mechanism	Ease
sRP	React with something to make a particle, or react with a particle	1
sNRP	Adsorption to a particle (Sticks to the particle surface without a chemical reaction)	4
pRP	Reaction with other particles, adsorption, coagulation, flocculation	2
pNRP	Adsorption, coagulation, flocculation	3

Chemical Phosphorus Removal with the Actiflo® Process
2015 ORWEF Short School, Clackamas Community College
Chris Maher, Operations Analyst
Rock Creek AWTF

Clean Water Services

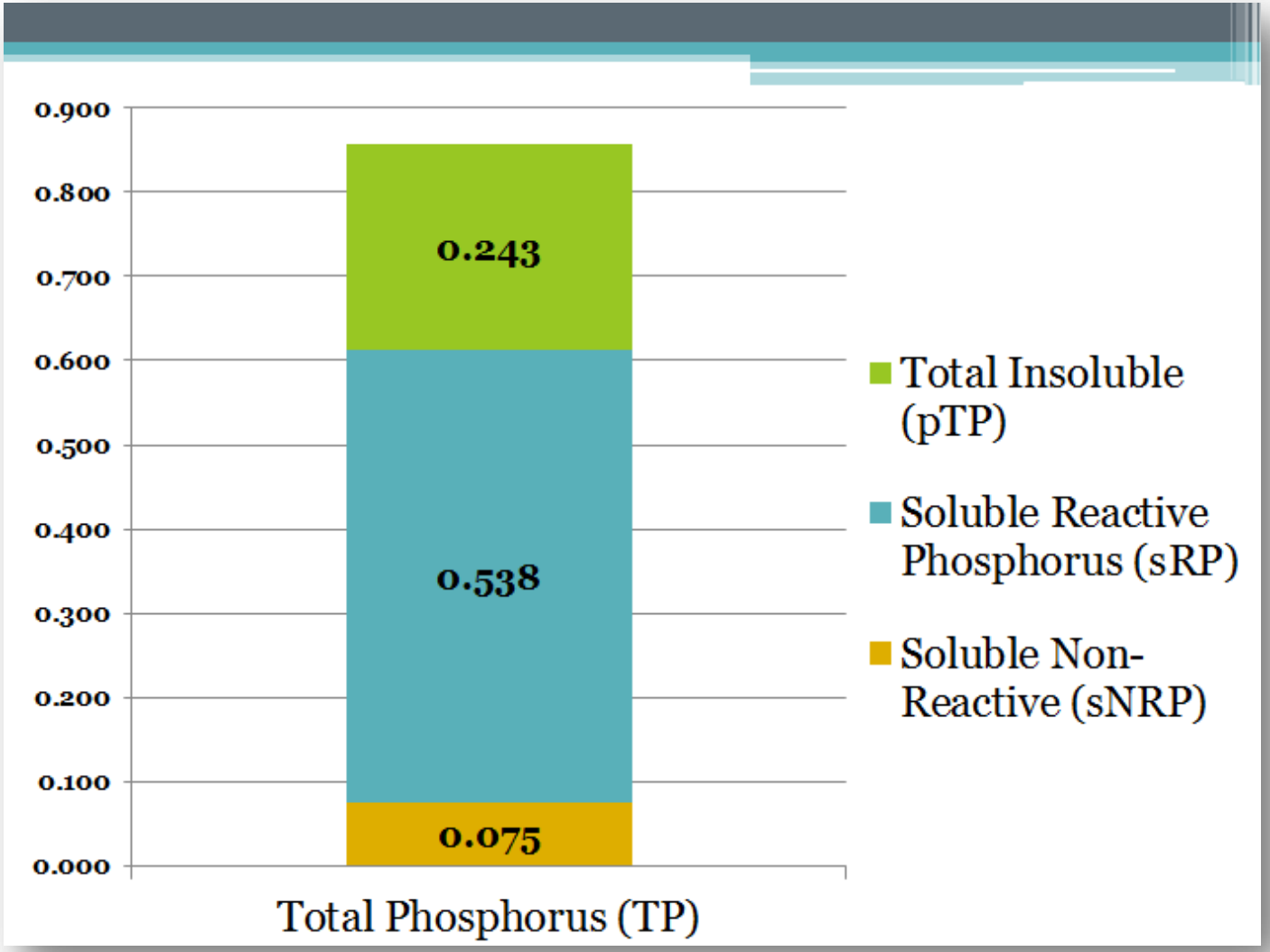
Fractions of P
Odds & Ends

Various Ways to Fractionize P

- Inorganic vs. organic
  - Requires two difference digestion methods
  - Chemical Treatment has real problems removing certain fractions of organic P
- Soluble vs. Insoluble (Particulate)
  - Filtered & unfiltered results
- Reactive vs. Non-Reactive
- Soluble NRP vs. Particulate NRP
  - All calculated values
- BIOAVAILABLE P

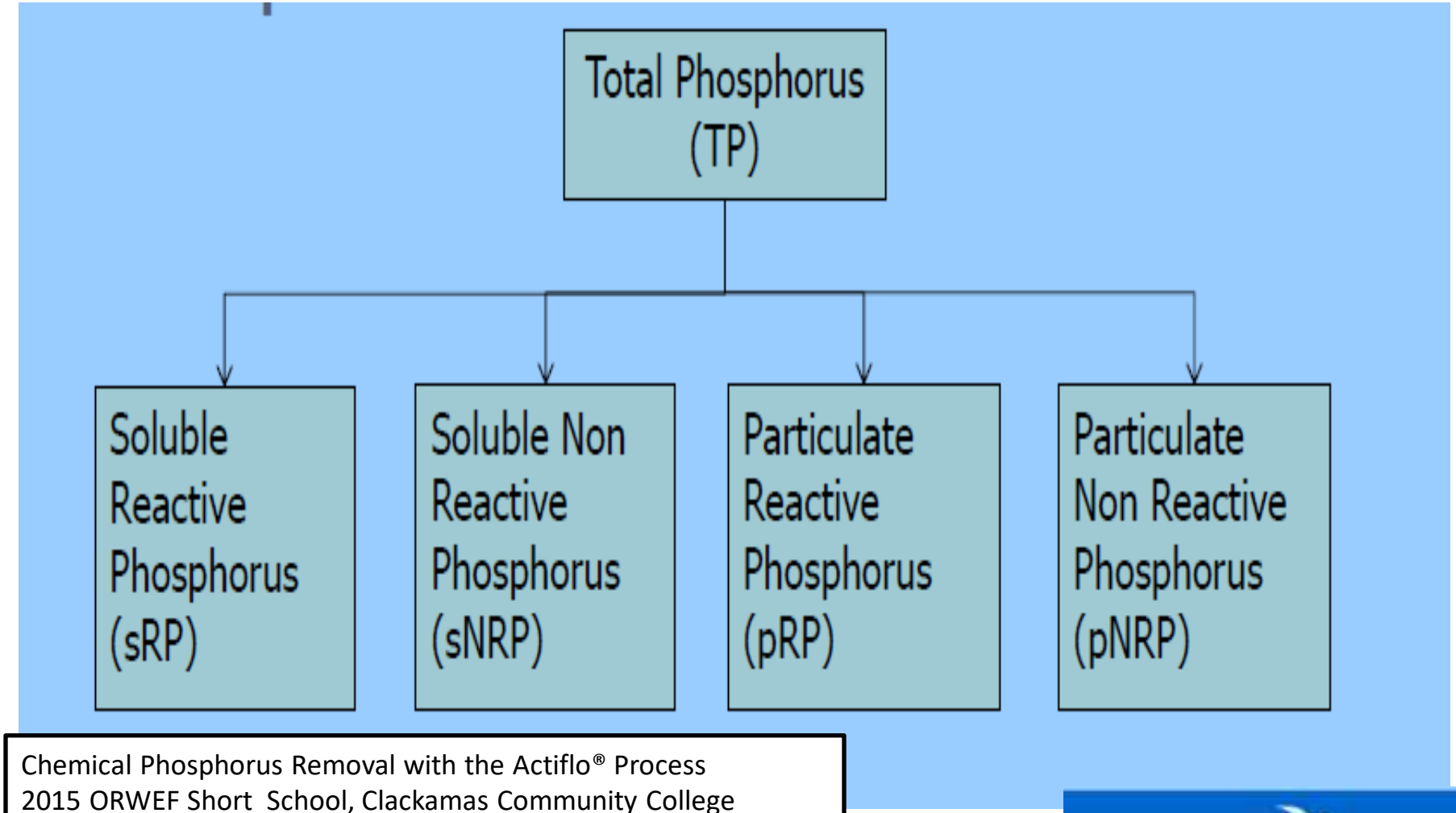
Soluble vs. Insoluble (Particulate)

Filtered & unfiltered results



Phosphorus Speciation by Autumn Fisher, Fond du Lac, WI

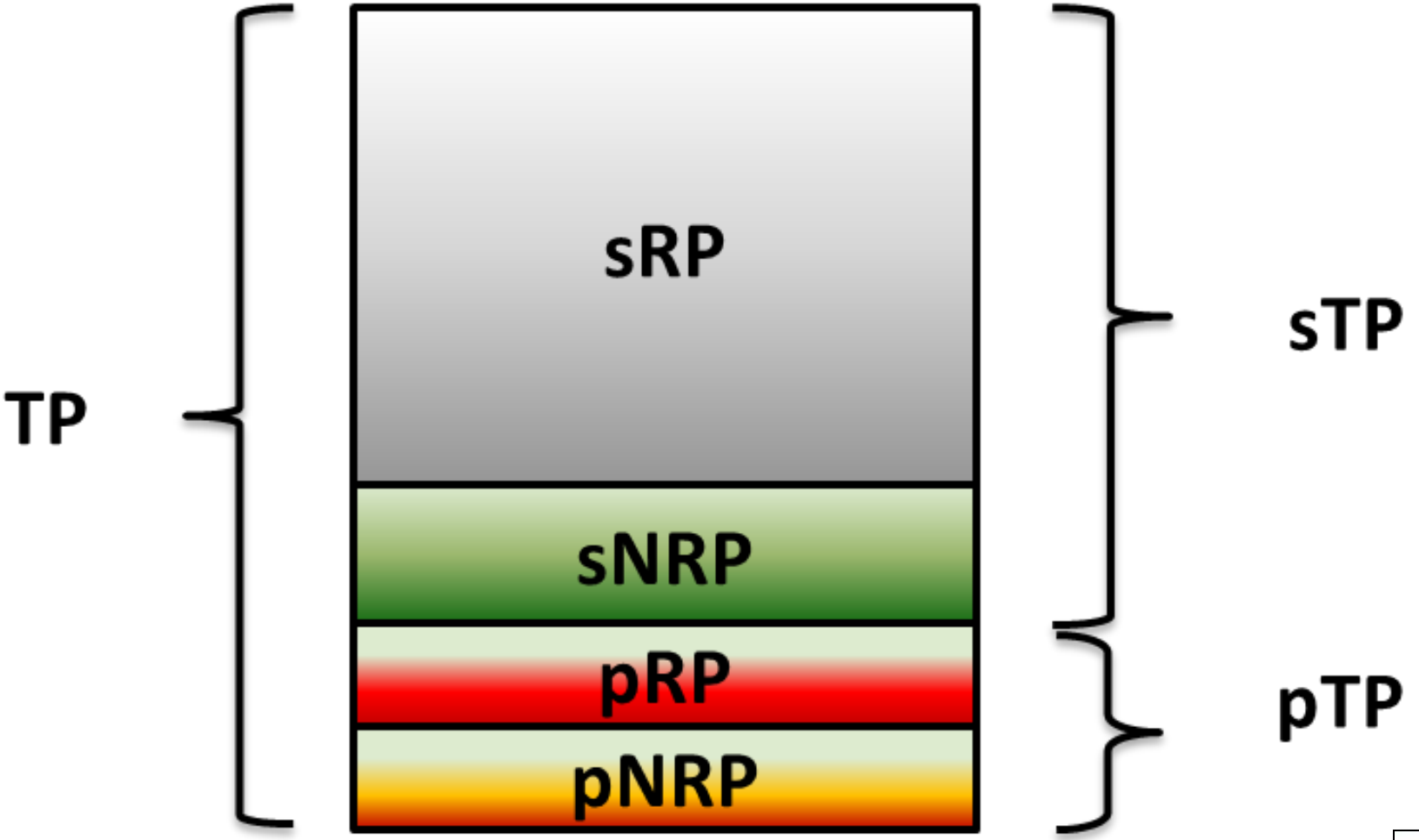
Soluble vs. Particulate (Reactive & Non-Reactive)



Chemical Phosphorus Removal with the Actiflo® Process
2015 ORWEF Short School, Clackamas Community College
Chris Maher, Operations Analyst
Rock Creek AWTF

Clean Water Services

SAME AS THIS



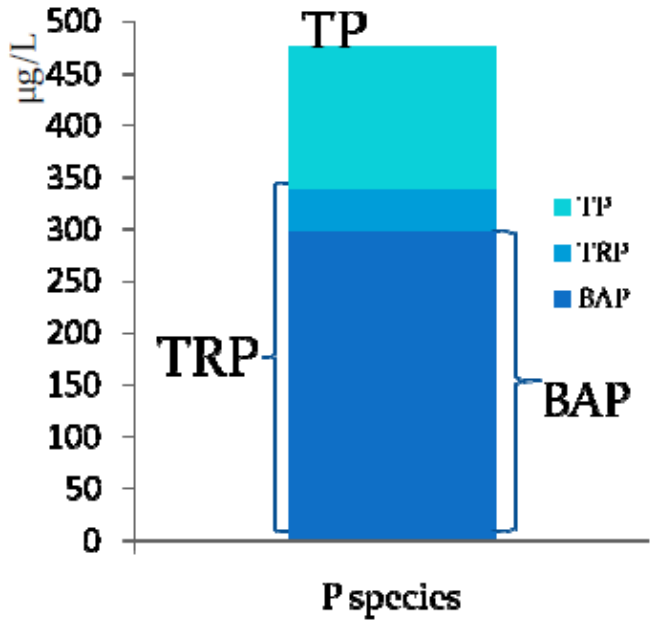
BioAvailable P – What is It?

- Algal available or **BIOAVAILABLE** phosphorus is P that is estimated to be available to organisms like algae that are present in a lake or river.
- This is usually estimated by a chemical test which is designed to measure the **soluble** P **&** the **particulate** P that are **EASILY AVAILABLE**.
- Measure of the P → immediate concern to water quality.

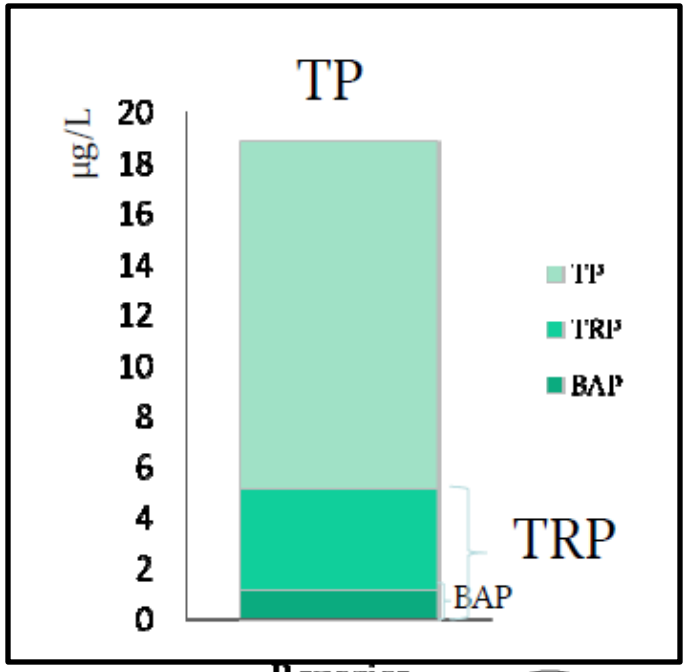
http://www.extension.umn.edu/agriculture/nutrient-management/phosphorus/the-nature-of-phosphorus/

Example Material Where Bioavailable P is being Evaluated

Bioavailable P (BAP) vs TP and TRP



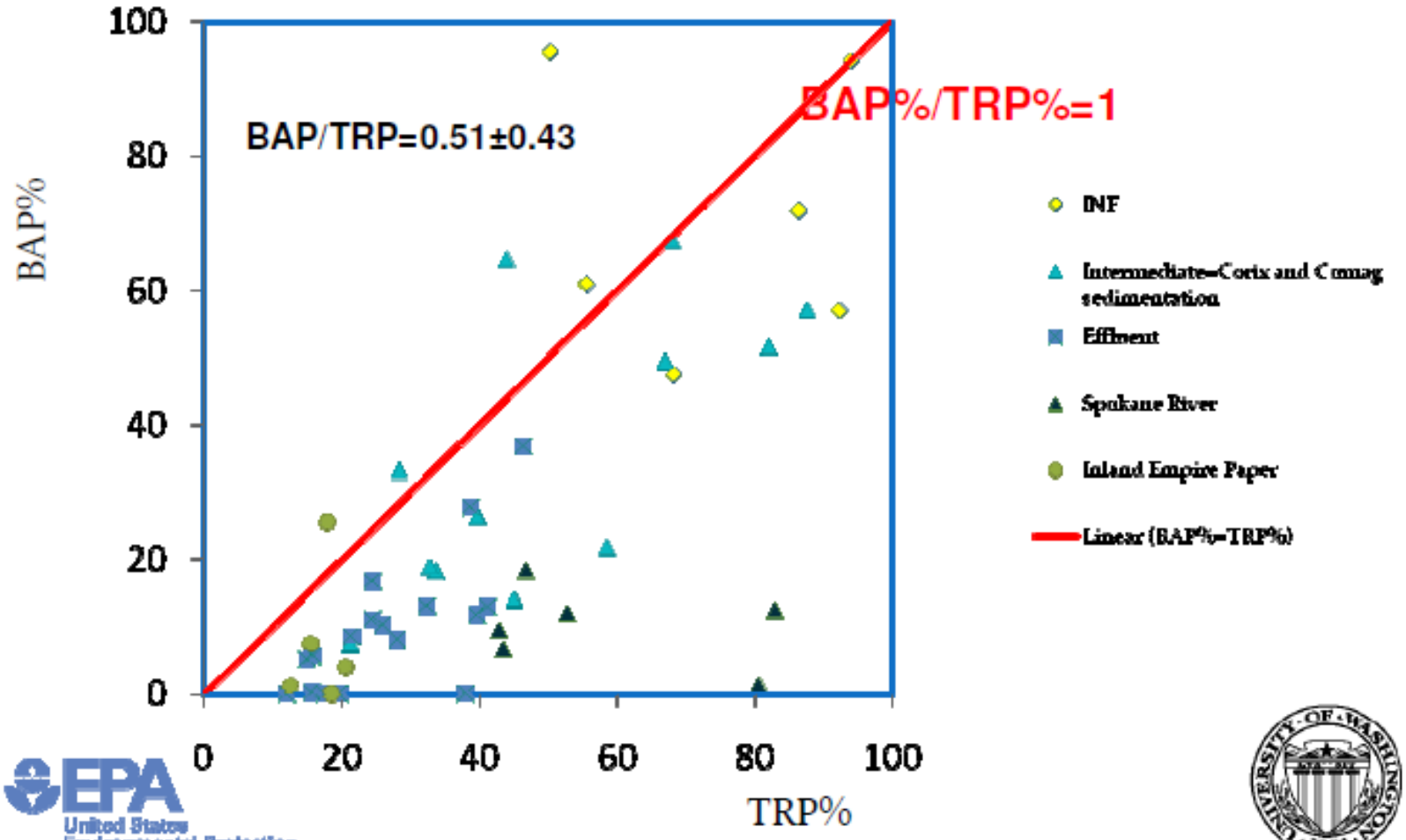
Plant Influent (n=4)



Filtered Effluent (n=4)

Study found Bioavailable P is LESS than Total Reactive Phosphorus

BAP is less than TRP



EPA United States Environmental Protection Agency

UNIVERSITY OF WASHINGTON 1861

OP2MYZ LLC

So Many Different Names !!!

Fraction of P	Abbrev.	Other names
Total Phosphorus	TP	
Total Reactive Phosphorus	tRP	Total Ortho-P, Total Orthophosphate as P, Total PO_4-P
Total Acid Hydrolysable Phosphorus	tAHP	
Total Non Reactive Phosphorus	tNRP	
Total Polymerized Phosphorus	tPoly	
Total Organic Phosphorus	tOP	
Total Particulate Phosphorus	pTP	
Particulate Reactive Phosphorus	pRP	Particulate Orthophosphorus, Particulate Orthophosphate as P
Particulate Organic Phosphorus	pOP	
Particulate Non Reactive Phosphorus	pNRP	
Particulate Polymerized Phosphorus	pPoly	
Particulate Acid Hydrolysable Phosphorus	pAHP	
Total Soluble Phosphorus	sTP	Total Dissolved Phosphorus
Soluble Acid Hydrolysable Phosphorus	sAHP	
Soluble Reactive Phosphorus	sRP	Soluble Orthophosphorus, Soluble Orthophosphate as P, Dissolved Reactive Phosphorus, Dissolved Orthophosphate as P, Dissolved Orthophosphorus, Dissolved PO_4-P, Soluble PO_4-P
Soluble Organic Phosphorus	sOP	Dissolved Organic Phosphorus, DOP
Soluble Non Reactive Phosphorus	sNRP	Disssolve Non-Reactive Phosphorus
Soluble Polymerized Phosphorus	sPoly	

Phosphorus Speciation

Same as Dividing Phosphorus into Different Fractions of P

P species

Same as Fractions of P

Examples of Various WWTP Experiences Results

Fond du Lac Experience

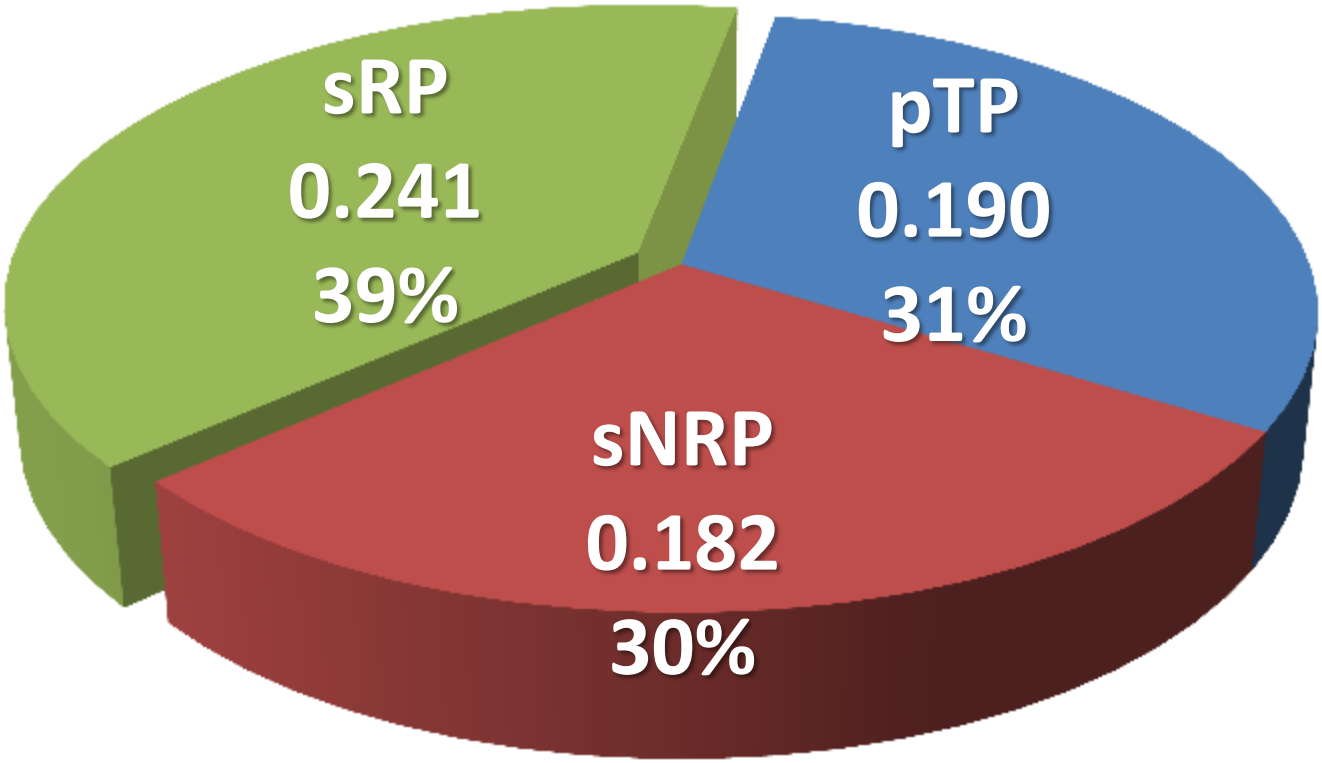
- Collected Data says……..
- Future WQBEL TP limit - **0.04** mg/l.
- Discovered Eff. sNRP fraction is **0.108** mg/l which is **0.068** mg/l **over the limit**
- sNRP is NOT EASILY REMOVED by chemical and/or EBPR
- Now studying smaller particles/solids are referred to as **colloidal solids**

Using Fort Atkinson Eff. P Data What Happens If?

Fort Atkinson - Fraction of Phosphorus in WWTP Effluent

Data from Fall of 2011

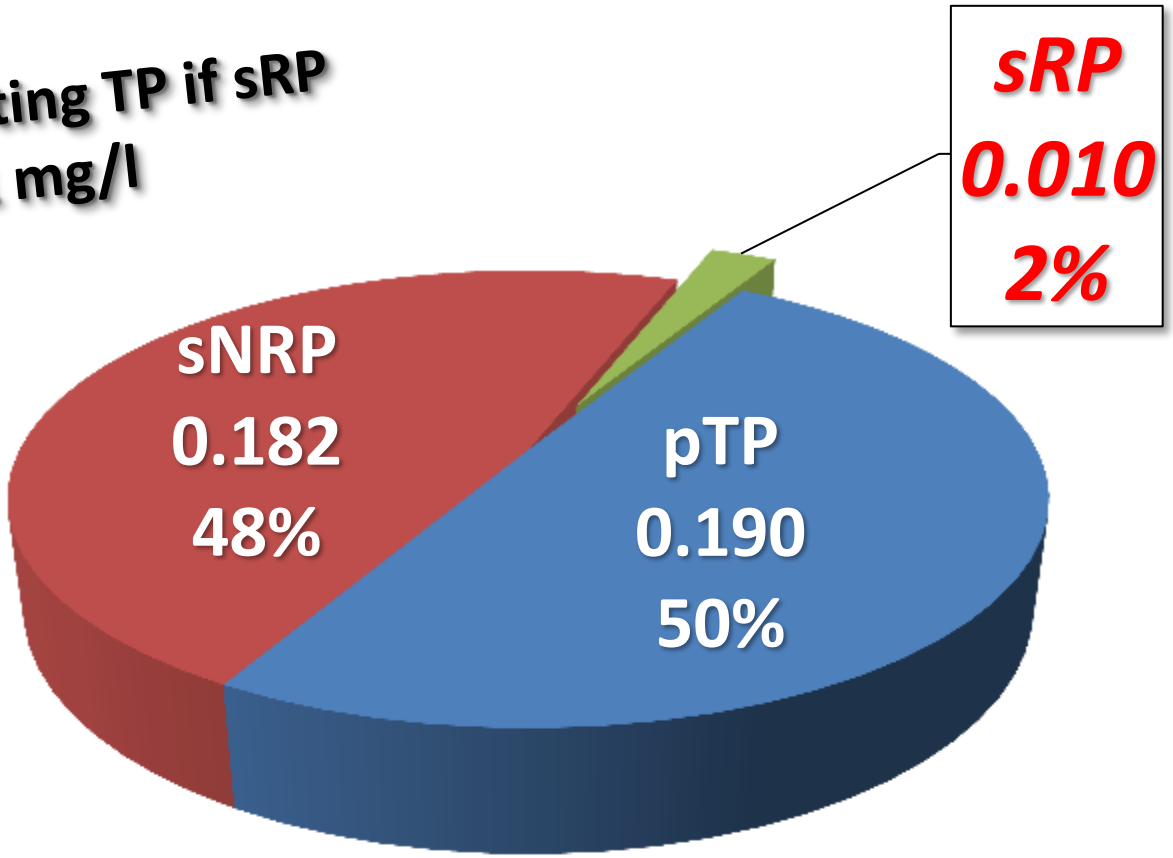
TP - 0.613 mg/l



Aug thru Oct 2011 - Average based on actual data

Fort Atkinson - Most Reactive P Removed by BNR

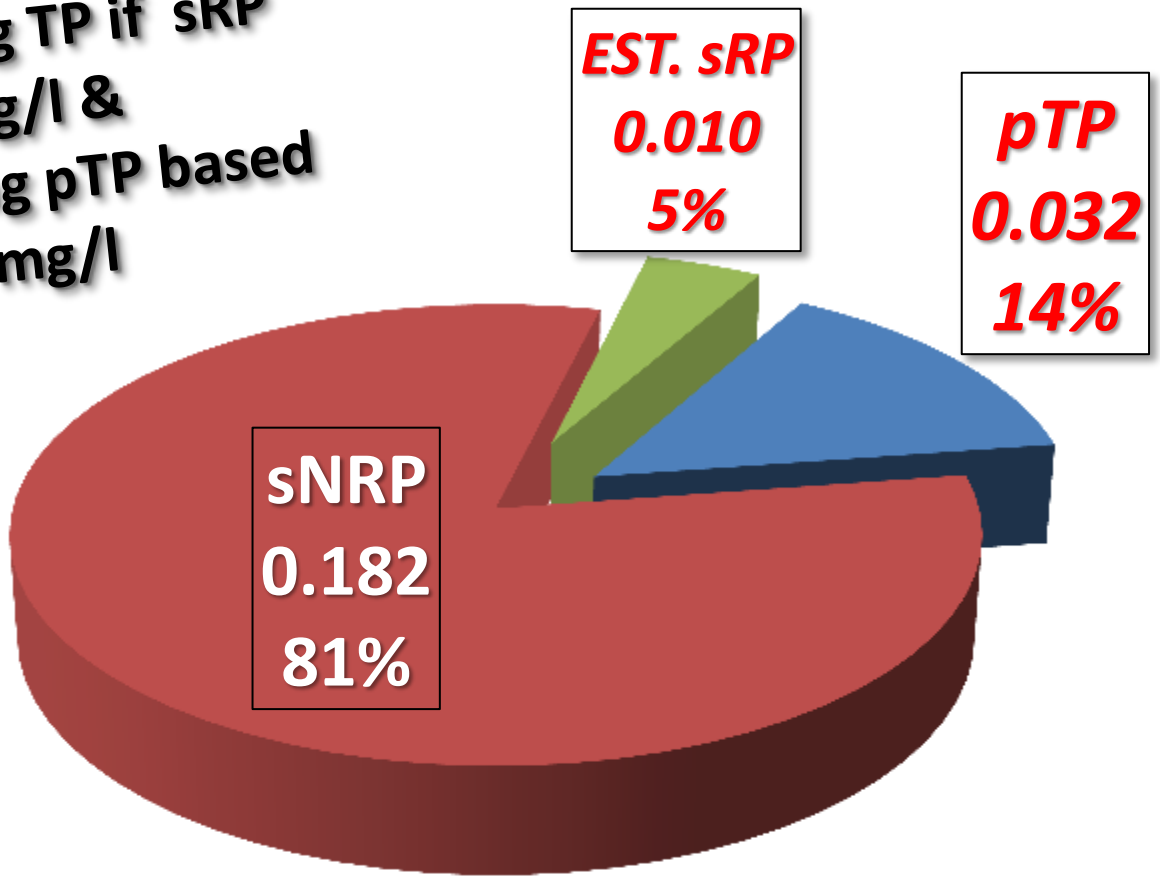
Estimating TP if sRP at 0.01 mg/l



Estimated TP, mg/l - 0.382

Fort Atkinson - Most Reactive P Removed by BNR and Effluent TSS Filtration

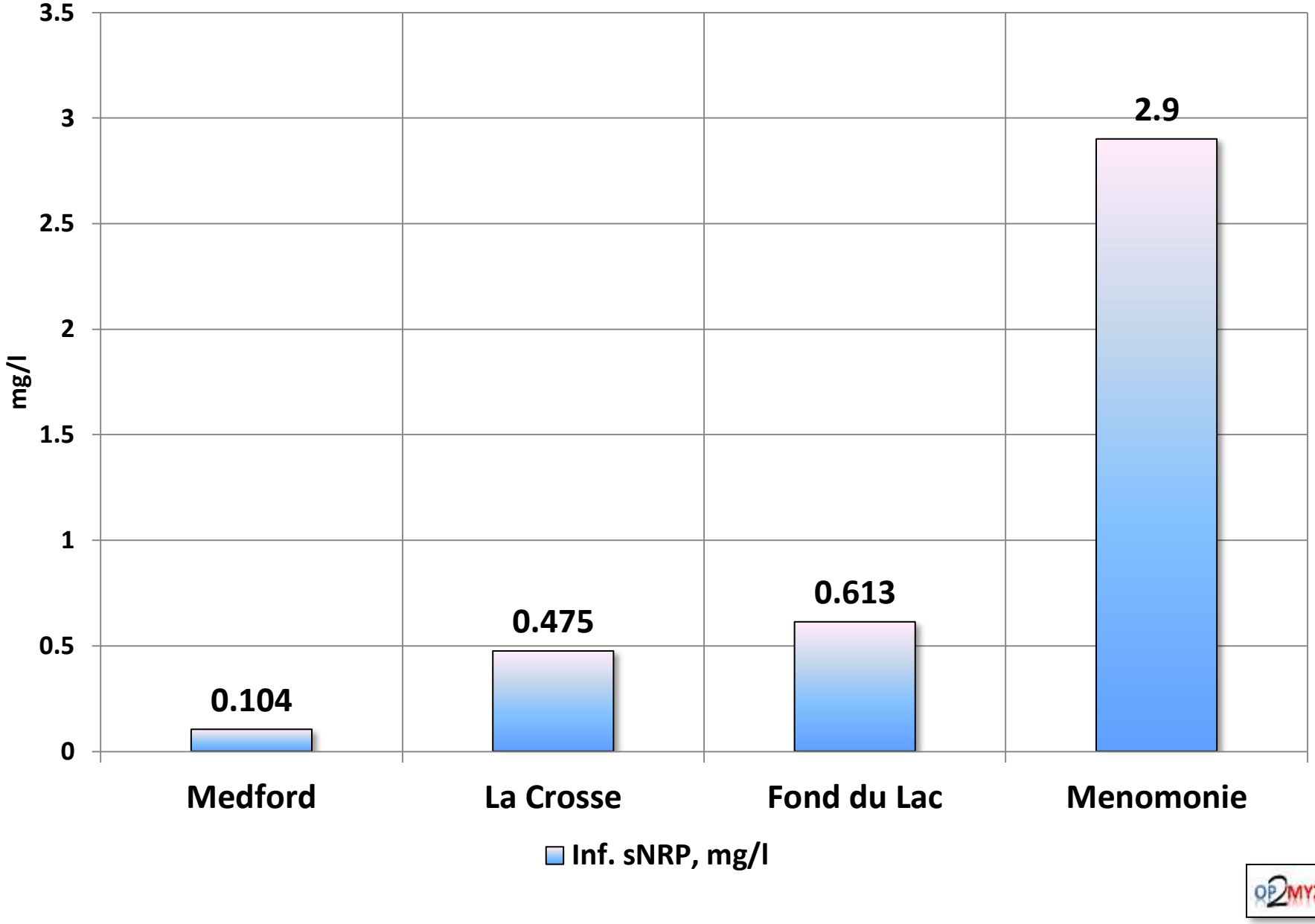
Estimating TP if sRP at 0.01 mg/l & Estimating pTP based on TSS 1 mg/l



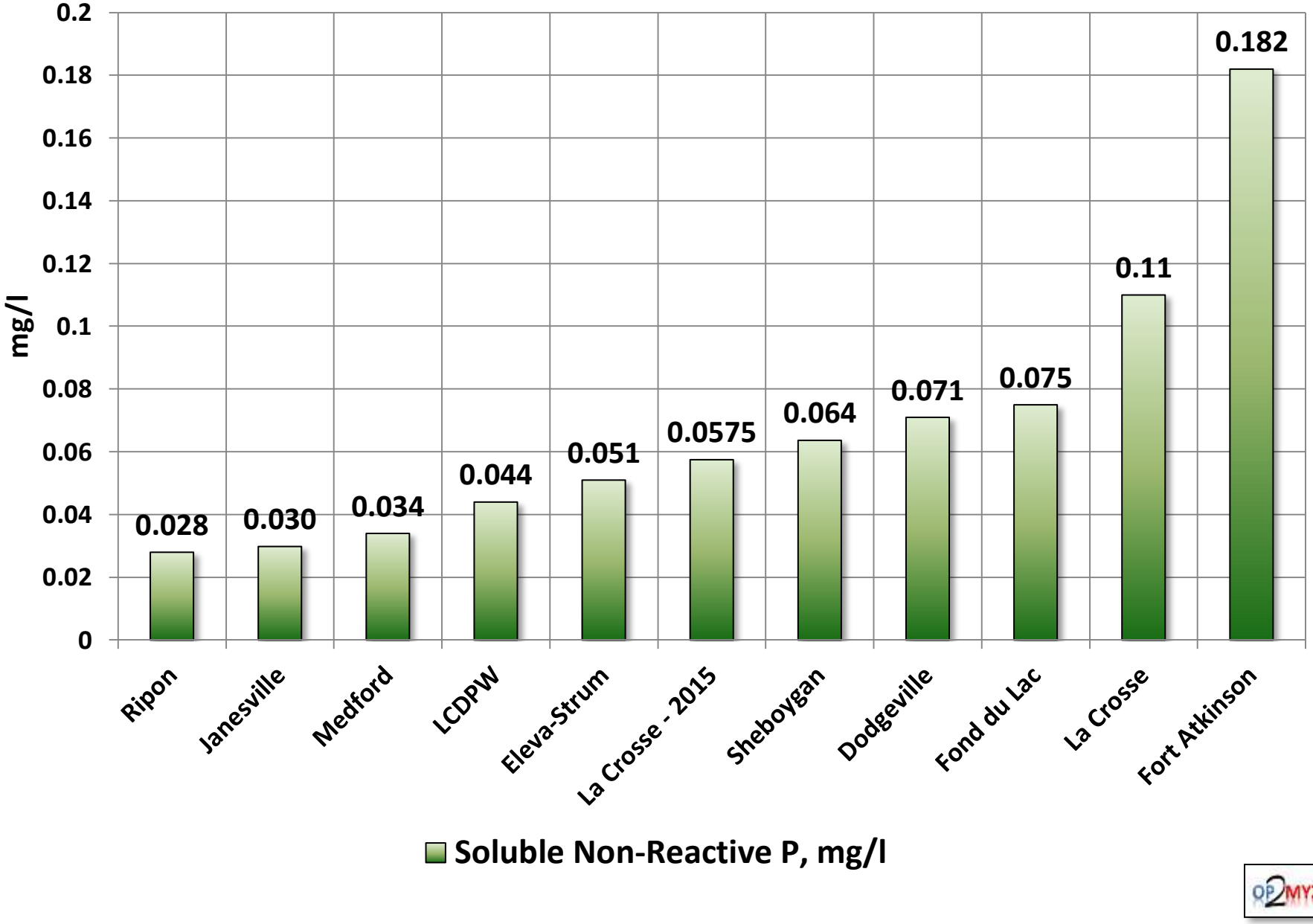
Before all Changes: TP - 0.613 mg/l

Estimated TP, mg/l - 0.224

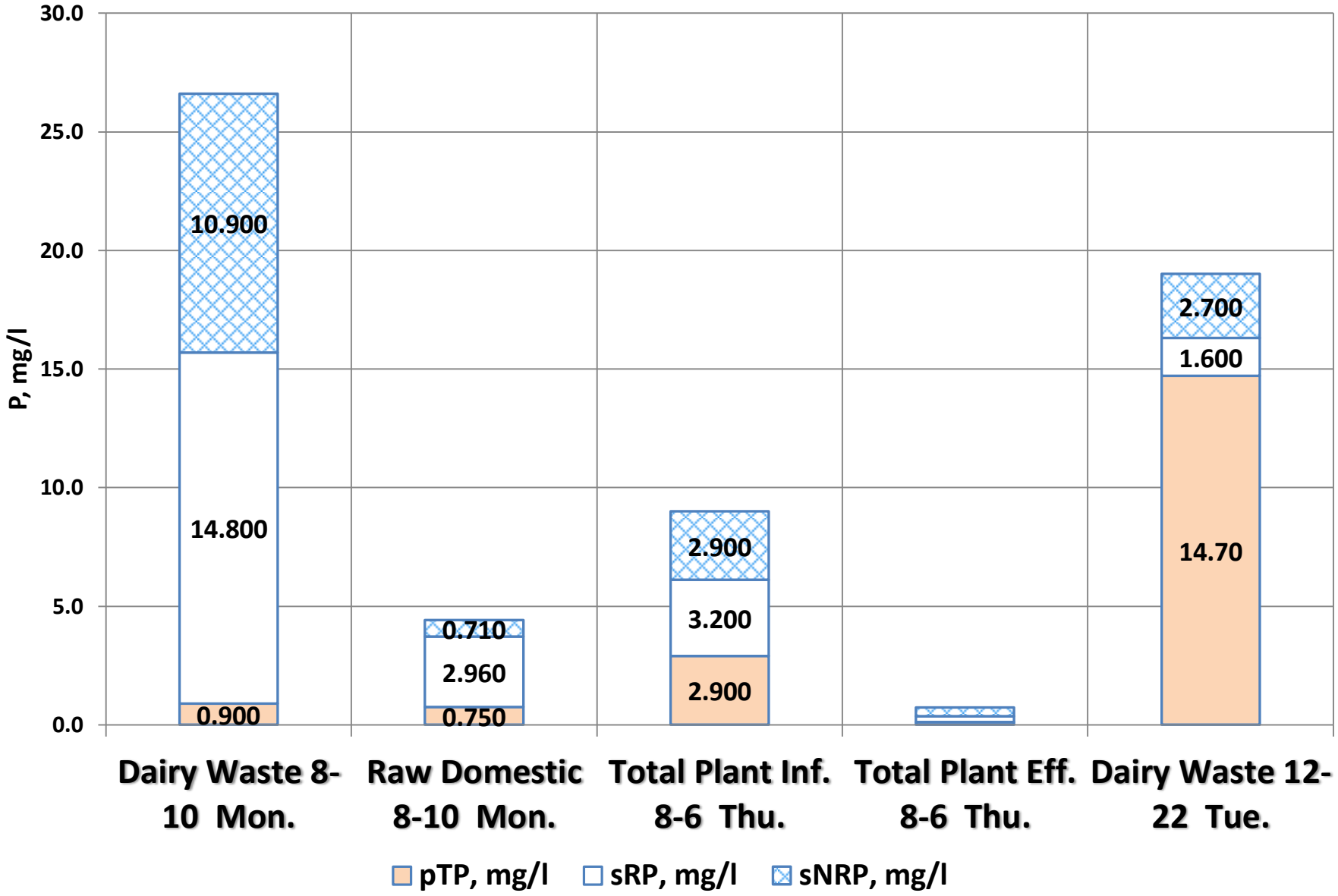
Inf. sNRP Survey

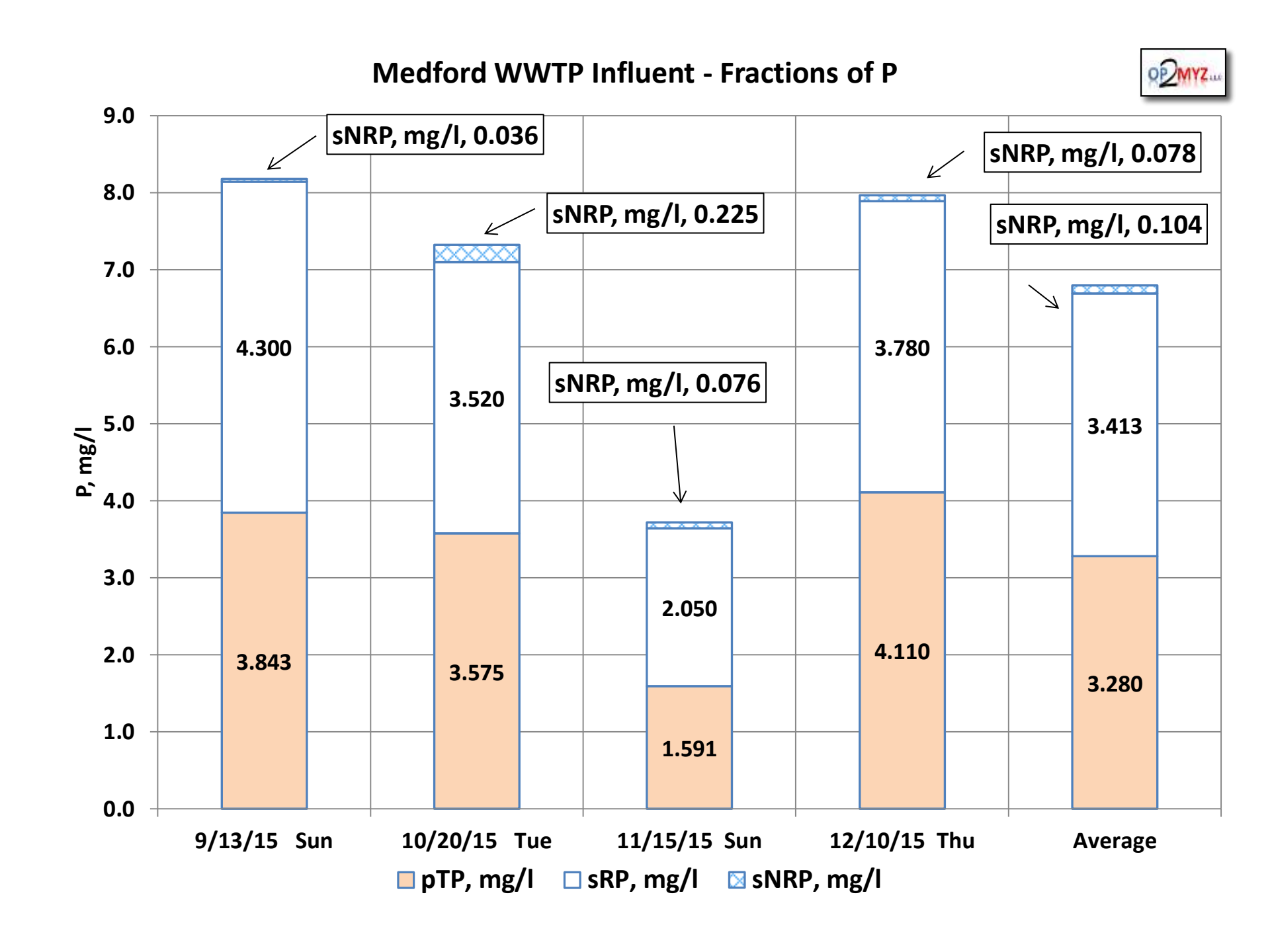


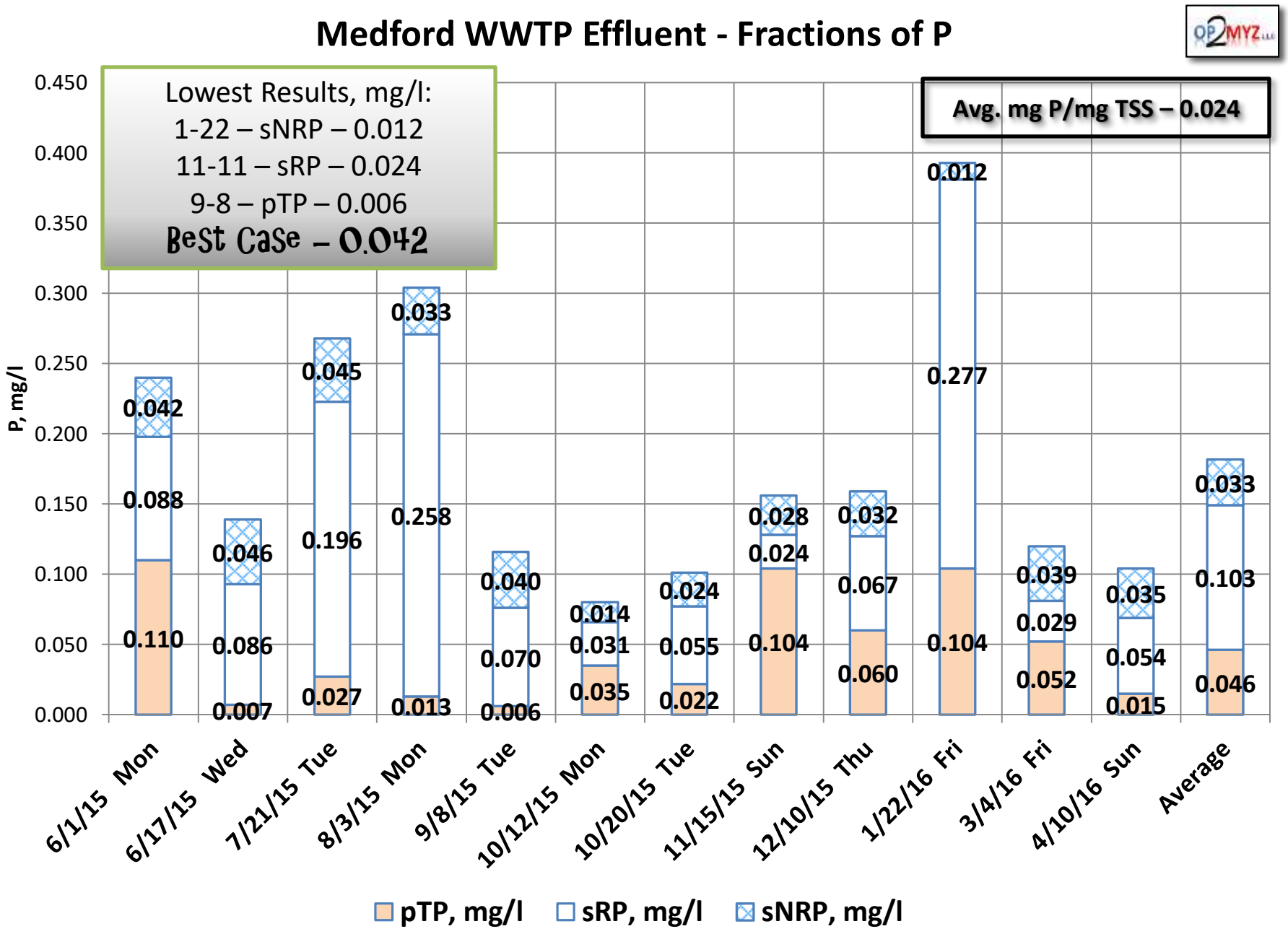
Eff - Soluble Non-Reactive P (sNRP) Survey

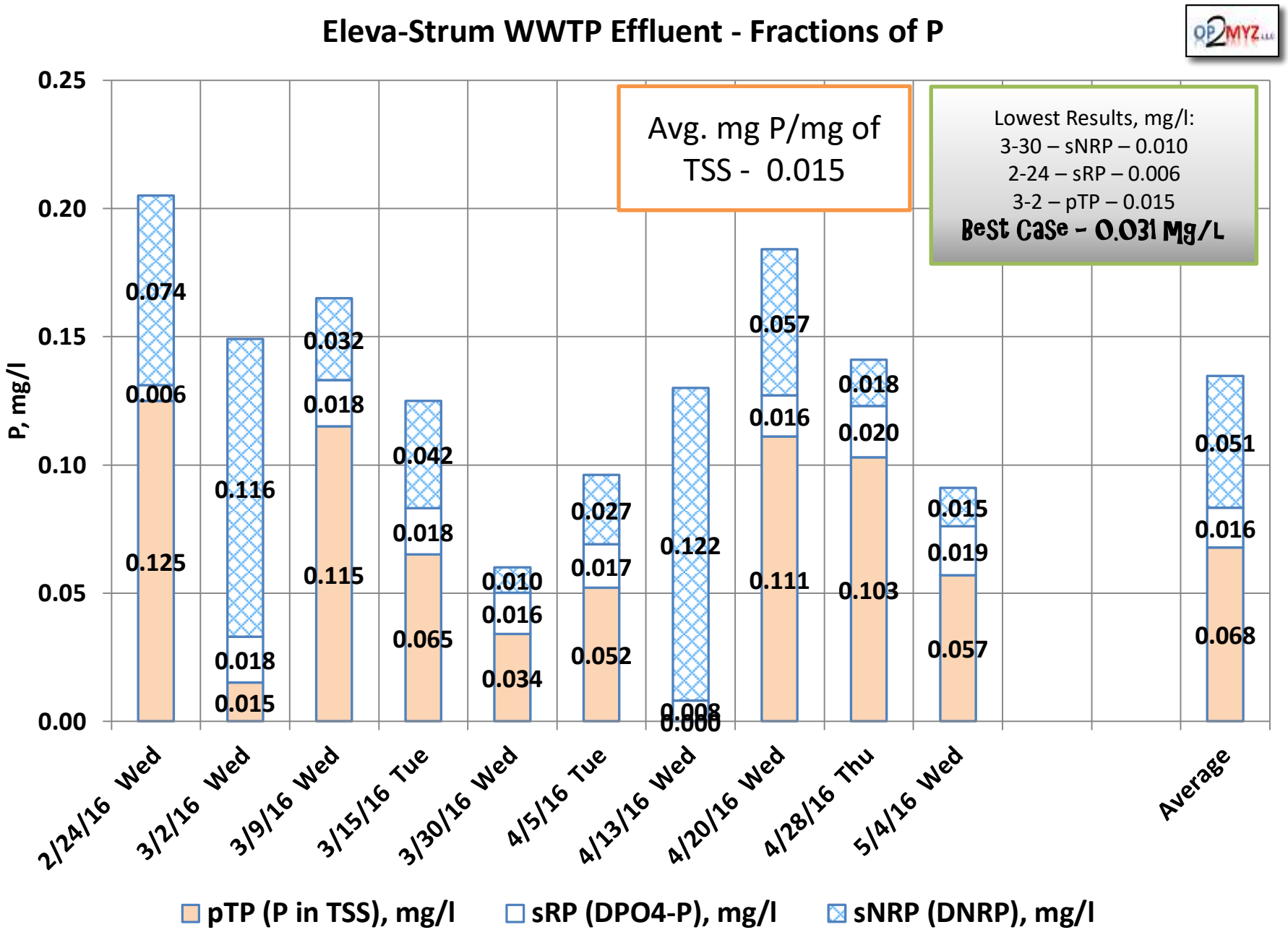


Menomonie WWTP Inf./Eff. - Fractions of P

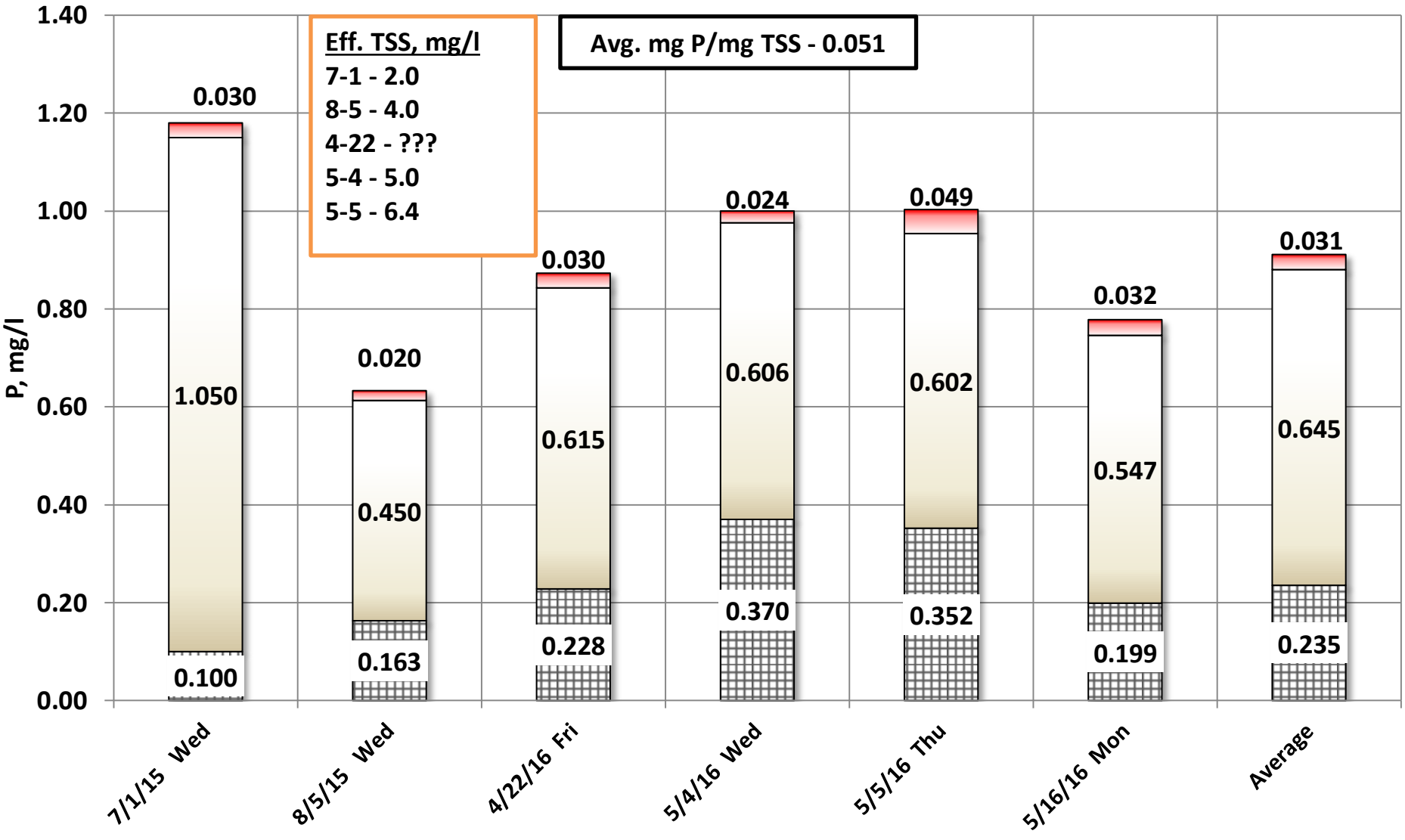


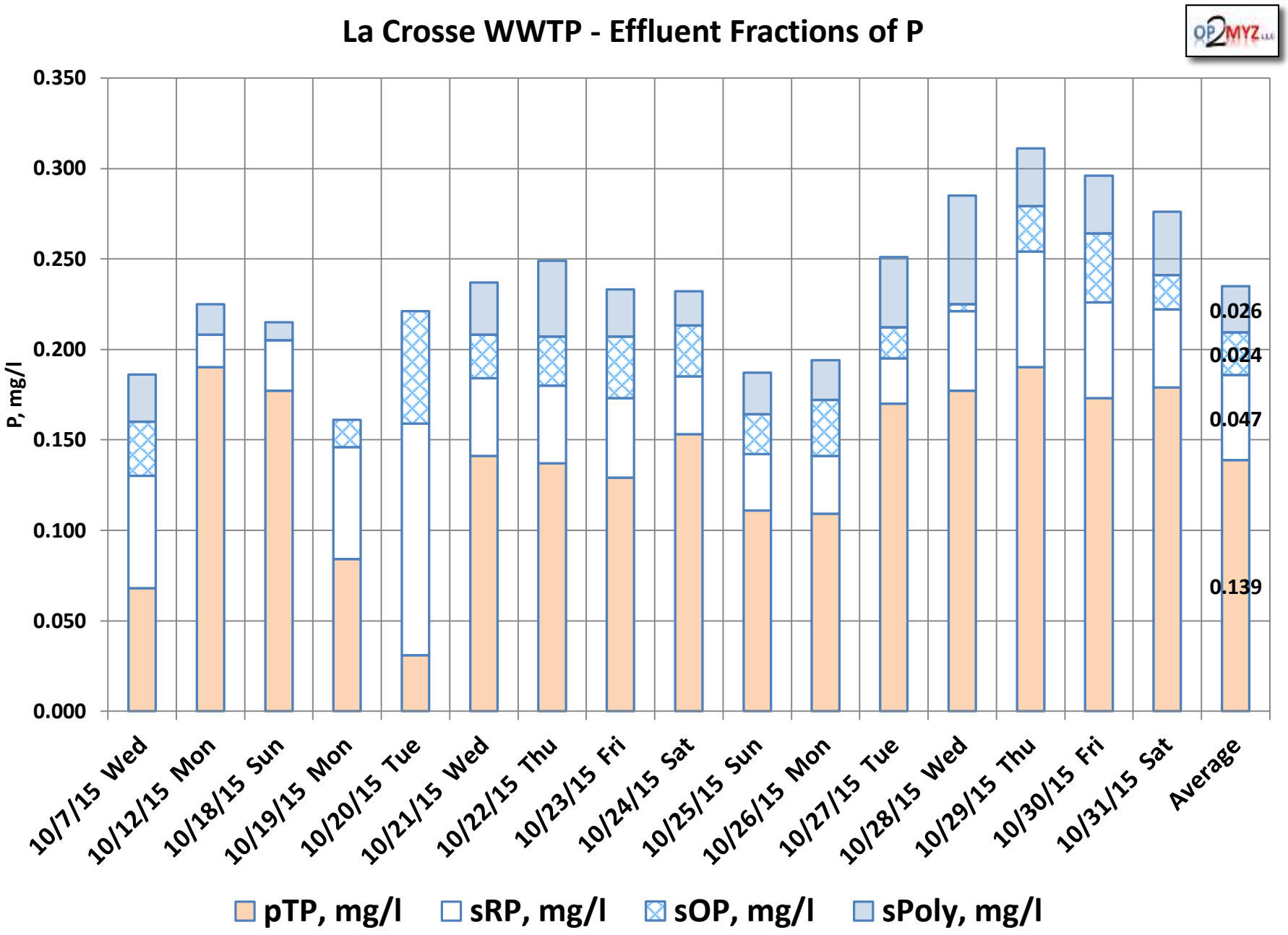

Medford WWTP Influent - Fractions of P
P, mg/l
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
sNRP, mg/l, 0.036
sNRP, mg/l, 0.225
sNRP, mg/l, 0.076
sNRP, mg/l, 0.078
sNRP, mg/l, 0.104
4.300
3.843
3.520
3.575
2.050
1.591
3.780
4.110
3.413
3.280
9/13/15 Sun
10/20/15 Tue
11/15/15 Sun
12/10/15 Thu
Average
pTP, mg/l
sRP, mg/l
sNRP, mg/l


Medford WWTP Effluent - Fractions of P
Lowest Results, mg/l:
1-22 – sNRP – 0.012
11-11 – sRP – 0.024
9-8 – pTP – 0.006
Best Case – 0.042
Avg. mg P/mg TSS – 0.024
P, mg/l
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0.042
0.088
0.110
0.046
0.086
0.007
0.045
0.196
0.027
0.033
0.258
0.013
0.040
0.070
0.006
0.014
0.031
0.035
0.024
0.055
0.022
0.028
0.024
0.104
0.032
0.067
0.060
0.012
0.277
0.104
0.039
0.029
0.052
0.035
0.054
0.015
0.033
0.103
0.046
6/1/15 Mon
6/17/15 Wed
7/21/15 Tue
8/3/15 Mon
9/8/15 Tue
10/12/15 Mon
10/20/15 Tue
11/15/15 Sun
12/10/15 Thu
1/22/16 Fri
3/4/16 Fri
4/10/16 Sun
Average
pTP, mg/l
sRP, mg/l
sNRP, mg/l


Eleva-Strum WWTP Effluent - Fractions of P
Avg. mg P/mg of TSS - 0.015
Lowest Results, mg/l:
3-30 – sNRP – 0.010
2-24 – sRP – 0.006
3-2 – pTP – 0.015
Best Case - 0.031 Mg/L
P, mg/l
0.25
0.20
0.15
0.10
0.05
0.00
0.074
0.006
0.125
0.116
0.018
0.015
0.032
0.018
0.115
0.042
0.018
0.065
0.010
0.016
0.034
0.027
0.017
0.052
0.122
0.008
0.000
0.057
0.016
0.111
0.018
0.020
0.103
0.015
0.019
0.057
0.051
0.016
0.068
2/24/16 Wed
3/2/16 Wed
3/9/16 Wed
3/15/16 Tue
3/30/16 Wed
4/5/16 Tue
4/13/16 Wed
4/20/16 Wed
4/28/16 Thu
5/4/16 Wed
Average
pTP (P in TSS), mg/l
sRP (DPO4-P), mg/l
sNRP (DNRP), mg/l

Antioch Eff. Fractions of P




La Crosse WWTP - Effluent Fractions of P
P, mg/l
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0.026
0.024
0.047
0.139
10/7/15 Wed
10/12/15 Mon
10/18/15 Sun
10/19/15 Mon
10/20/15 Tue
10/21/15 Wed
10/22/15 Thu
10/23/15 Fri
10/24/15 Sat
10/25/15 Sun
10/26/15 Mon
10/27/15 Tue
10/28/15 Wed
10/29/15 Thu
10/30/15 Fri
10/31/15 Sat
Average
pTP, mg/l
sRP, mg/l
sOP, mg/l
sPoly, mg/l

Sources of Info

- WEFTEC 2010: Comparison of Phosphorus Fractionation in Effluents from Different Wastewater Treatment Processes
- Water Science & Technology 2011: Treatability and fate of various phosphorus fractions in different wastewater treatment process
- WEFTEC 2008: Not so fat! The impact of recalcitrant phosphorus on the ability to meet low phosphorus limits
- 2010 EPA Technology Transfer Seminar
- 2015 ORWEF Short School, Clackamas Community College, Chris Maher
- Phosphorus Speciation by Autumn Fischer, Fond du Lac, WI
- From Hach Method for ACID HYDROLYZABLE PHOSPHORUS
- Data from Medford, Fort Atkinson, La Crosse, Eleva-Strum, Fond du Lac, Menomonie & Antioch (IL) WWTPs

Thank You

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