What/How/Why Fractions of P

By Op2Myz, LLC
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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 you get the Simpler Fractions of P???
Total Phosphorus
Persulfate Digestion
Direct Colorimetric Method

TP
Total Soluble Phosphorus
Filter (0.45 Micron)/Persulfate Digestion
Direct Colorimetric Method
Total Particulate Phosphorus
TP minus sTP

TP

pTP

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
# List of Fractions of P

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

tAHP

True tAHP

Organic P bleed thru
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

- Total particulate phosphorus (pTP)
  - Includes pRP, pPoly and pOP

- Soluble reactive phosphorus (sRP)
- Soluble non-reactive phosphorus (sNRP)

- Total soluble phosphorus (sTP)
  - Includes sPoly and sOP

- Total Phosphorus (TP)
Fractions of $\text{TOTAL}(t) P$
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 \( \text{PARTICULATE} \ (p) \ P \)
Total Particulate Phosphorus (pTP)

TP - sTP

TP & sTP are direct analysis
Particulate Reactive Phosphorus (pRP)

tRP & sRP are direct analysis
Particulate Organic Phosphorus (pOP)

\[ tOP = TP - tAHP \]
\[ sOP = sTP - sAHP \]

TP, tAHP, sTP & sAHP are all direct analysis
Particulate Non-Reactive Phosphorus (pNRP)

\[ \text{tNRP} = \text{TP} - \text{tRP} \]
\[ \text{sNRP} = \text{sTP} - \text{sRP} \]

TP, tRP, sTP, & sRP are all direct analysis.
Particulate Polymerized Phosphorus (pPoly)

\[ t_{Poly} = t_{AHP} - t_{RP} \]

\[ s_{Poly} = s_{AHP} - s_{RP} \]
tAHP & sAHP are direct analysis

pAHP

tAHP - sAHP
Fractions of SOLUBLE (s) P
Total Soluble Phosphorus (sTP)

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

- Includes pRP, pPoly and pOP
- Includes sPoly and sOP

- Total particulate phosphorus (pTP)
- Soluble reactive phosphorus (sRP)
- Soluble non-reactive phosphorus (sNRP)
- Total soluble phosphorus (sTP)
- Includes sPoly and sOP
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?
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
A day with high Eff. TSS

VERY Low sRP – EBPR Working Well

Higher then normal sNRP - Look for Source

Having an Avg. Helps
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

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

- Total Phosphorus (TP)
  - Soluble Reactive Phosphorus (sRP)
  - Soluble Non Reactive Phosphorus (sNRP)
  - Particulate Reactive Phosphorus (pRP)
  - Particulate Non Reactive Phosphorus (pNRP)
SAME AS THIS

TP

sRP

sNRP

pRP

pNRP

sTP

pTP
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

- TP
- TRP
- BAP

Plant Influent (n=4)

Filtered Effluent (n=4)

United States Environmental Protection Agency

EPA

[Graph showing TP, TRP, and BAP concentrations in Plant Influent and Filtered Effluent]
Study found Bioavailable P is LESS than Total Reactive Phosphorus.

BAP is less than TRP

\[
\frac{\text{BAP}}{\text{TRP}} = 0.51 \pm 0.43
\]

\[
\frac{\text{BAP\%}}{\text{TRP\%}} = 1
\]

- INF
- Intermediate-Cortex and Connag sedimentation
- Effluent
- Spokane River
- Inland Empire Paper

Linear (BAP\% = TRP\%)

United States Environmental Protection Agency

University of Washington
### So Many Different Names !!!

<table>
<thead>
<tr>
<th>Fraction of P</th>
<th>Abbrev.</th>
<th>Other names</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Phosphorus</td>
<td>TP</td>
<td>Total Ortho-P, Total Orthophosphate as P, Total $PO_4$-P</td>
</tr>
<tr>
<td>Total Reactive Phosphorus</td>
<td>tRP</td>
<td>Particulate Orthophosphorus, Particulate Orthophosphate as P</td>
</tr>
<tr>
<td>Total Acid Hydrolysable Phosphorus</td>
<td>tAHP</td>
<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>Total Polymerized Phosphorus</td>
<td>tPoly</td>
<td></td>
</tr>
<tr>
<td>Total Organic Phosphorus</td>
<td>tOP</td>
<td></td>
</tr>
<tr>
<td>Total Particulate Phosphorus</td>
<td>pTP</td>
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</tr>
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<td>Particulate Orthophosphorus, Particulate Orthophosphate as P</td>
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<tr>
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<td>pAHP</td>
<td></td>
</tr>
<tr>
<td>Total Soluble Phosphorus</td>
<td>sTP</td>
<td>Total Dissolved Phosphorus</td>
</tr>
<tr>
<td>Soluble Acid Hydrolysable Phosphorus</td>
<td>sAHP</td>
<td></td>
</tr>
<tr>
<td>Soluble Reactive Phosphorus</td>
<td>sRP</td>
<td>Soluble Orthophosphorus, Soluble Orthophosphate as P, Dissolved Reactive Phosphorus, Dissolved Orthophosphorus, Dissolved $PO_4$-P, Soluble $PO_4$-P</td>
</tr>
<tr>
<td>Soluble Organic Phosphorus</td>
<td>sOP</td>
<td>Dissolved Organic Phosphorus, DOP</td>
</tr>
<tr>
<td>Soluble Non Reactive Phosphorus</td>
<td>sNRP</td>
<td>Dissolved Non-Reactive Phosphorus</td>
</tr>
<tr>
<td>Soluble Polymerized Phosphorus</td>
<td>sPoly</td>
<td></td>
</tr>
</tbody>
</table>
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

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

<table>
<thead>
<tr>
<th>Location</th>
<th>mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medford</td>
<td>0.104</td>
</tr>
<tr>
<td>La Crosse</td>
<td>0.475</td>
</tr>
<tr>
<td>Fond du Lac</td>
<td>0.613</td>
</tr>
<tr>
<td>Menomonie</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Inf. sNRP, mg/l
Eff - Soluble Non-Reactive P (sNRP) Survey

Soluble Non-Reactive P, mg/l

- Ripon: 0.028
- Janesville: 0.030
- Medford: 0.034
- LCDPW: 0.044
- Eleva-Strum: 0.051
- La Crosse - 2015: 0.0575
- Sheboygan: 0.064
- Dodgeville: 0.071
- Fond du Lac: 0.075
- La Crosse: 0.11
- Fort Atkinson: 0.182
Menomonie WWTP Inf./Eff. - Fractions of P

Dairy Waste 8-10 Mon. 14.800
Raw Domestic 8-10 Mon. 0.900 2.960 0.750
Total Plant Inf. 8-6 Thu. 2.900 3.200
Total Plant Eff. 8-6 Thu. 2.700
Dairy Waste 12-22 Tue. 14.70 1.600

pTP, mg/l  sRP, mg/l  sNRP, mg/l
Medford WWTP Influent - Fractions of P

- **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**

**P, mg/l**

- **9/13/15 Sun**
  - pTP, mg/l: 3.843
  - sRP, mg/l: 3.575
  - sNRP, mg/l: 1.591

- **10/20/15 Tue**
  - pTP, mg/l: 4.300
  - sRP, mg/l: 3.520
  - sNRP, mg/l: 2.050

- **11/15/15 Sun**
  - pTP, mg/l: 1.591

- **12/10/15 Thu**
  - pTP, mg/l: 3.780
  - sRP, mg/l: 4.110
  - sNRP, mg/l: 3.413

**Average**

- **pTP, mg/l**: 3.280
- **sRP, mg/l**: 3.413
- **sNRP, mg/l**: 3.280
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
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

pTP (P in TSS), mg/l
sRP (DPO4-P), mg/l
sNRP (DNRP), mg/l
Antioch Eff. Fractions of P

Eff. TSS, mg/l
- 7-1 - 2.0
- 8-5 - 4.0
- 4-22 - ???
- 5-4 - 5.0
- 5-5 - 6.4

Avg. mg P/mg TSS - 0.051

0.030
1.050
0.020
0.450
0.030
0.615
0.024
0.606
0.049
0.602
0.032
0.547
0.031
0.645

P, mg/l

0.100
0.163
0.228
0.370
0.352
0.199
0.235

7/1/15 Wed
8/5/15 Wed
4/22/16 Fri
5/4/16 Wed
5/5/16 Thu
5/16/16 Mon
Average

pTP - Total Particulate P, mg/l
sRP - Dissolved Reactive P, mg/l
sNRP - Dissolved Non-Reactive P, mg/l
La Crosse WWTP - Effluent Fractions of P

- pTP, mg/l
- sRP, mg/l
- sOP, mg/l
- sPoly, mg/l

Average:
- pTP: 0.139 mg/l
- sRP: 0.047 mg/l
- sOP: 0.026 mg/l
- sPoly: 0.024 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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