Optimizing Chemical Phosphorus Removal

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HDR Engineering

2013 Technical Conference and Exposition
Ohio Water Environment Association (OWEA)
Mason, OH
June 18-20, 2013

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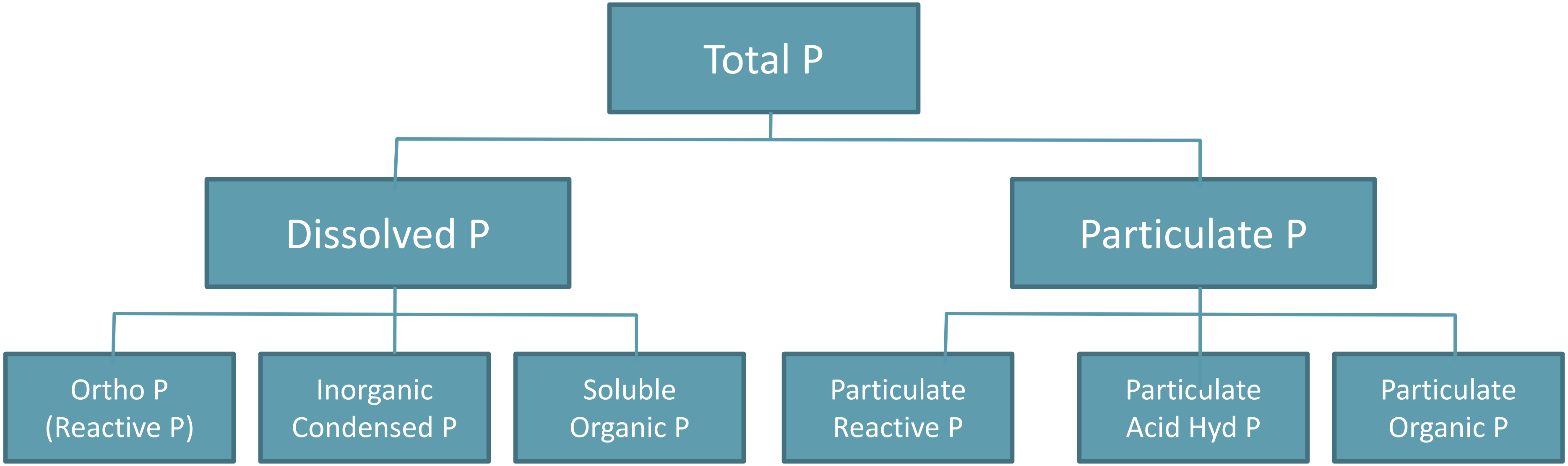
Agenda

- Chemical Phosphorus Removal Basics
- Phosphorus Species
- Performance
- Opportunities for Optimization

Phosphorus Species



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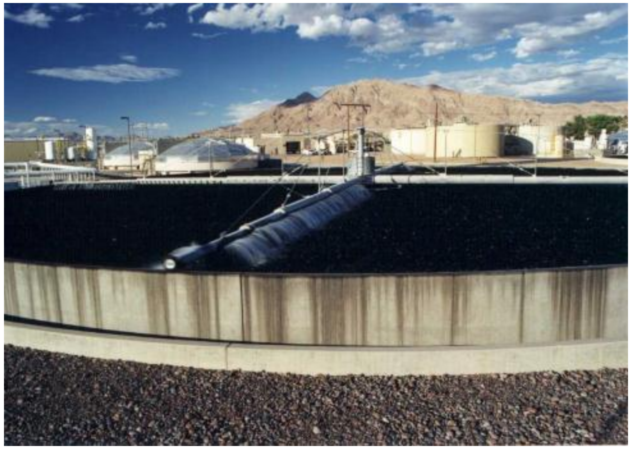
Fundamental Principle of Phosphorus Removal

There is no airborne (gaseous) form of phosphorus

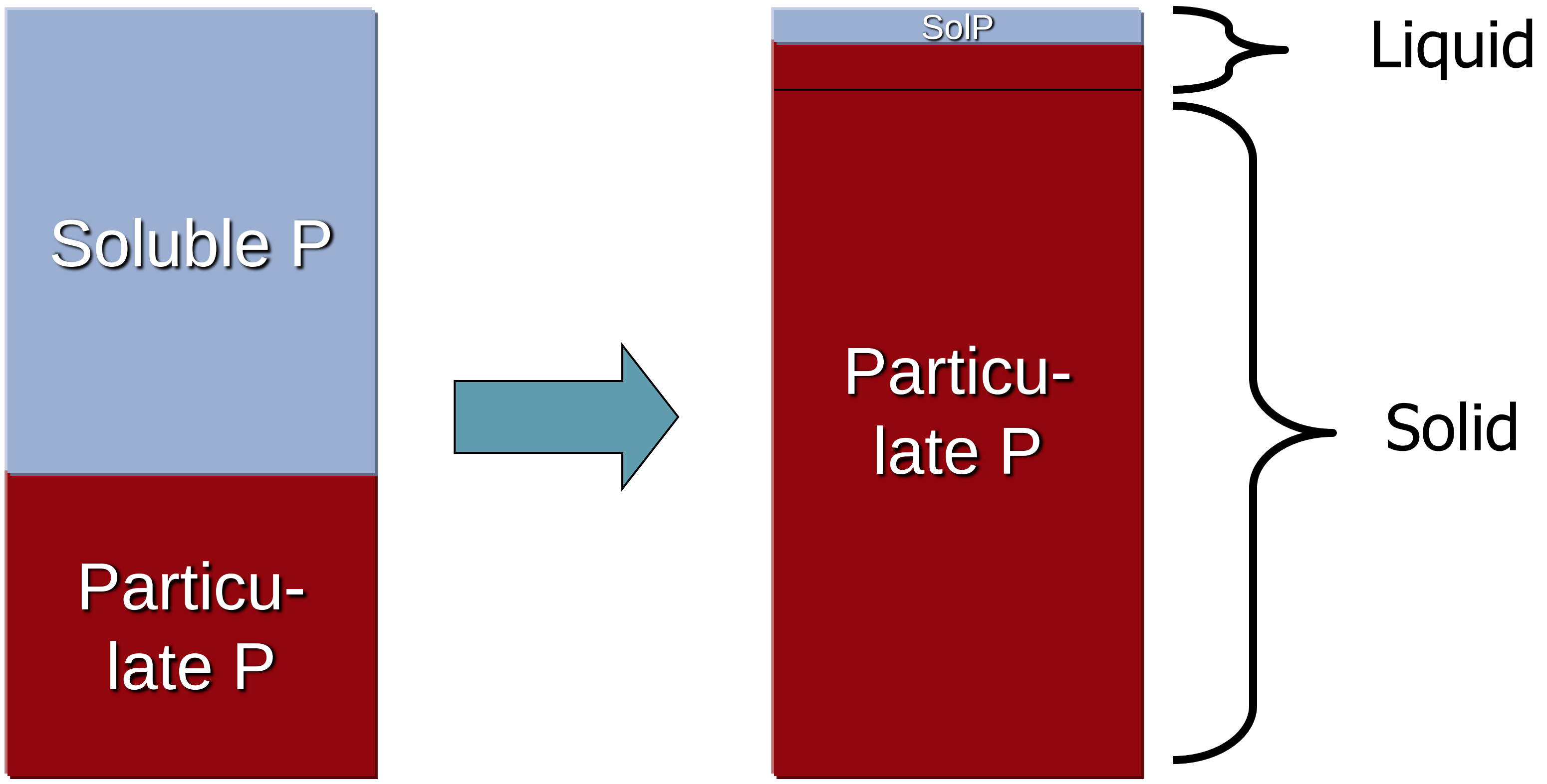
Fundamental Principle of Phosphorus Removal

There is no airborne (gaseous) form of phosphorus

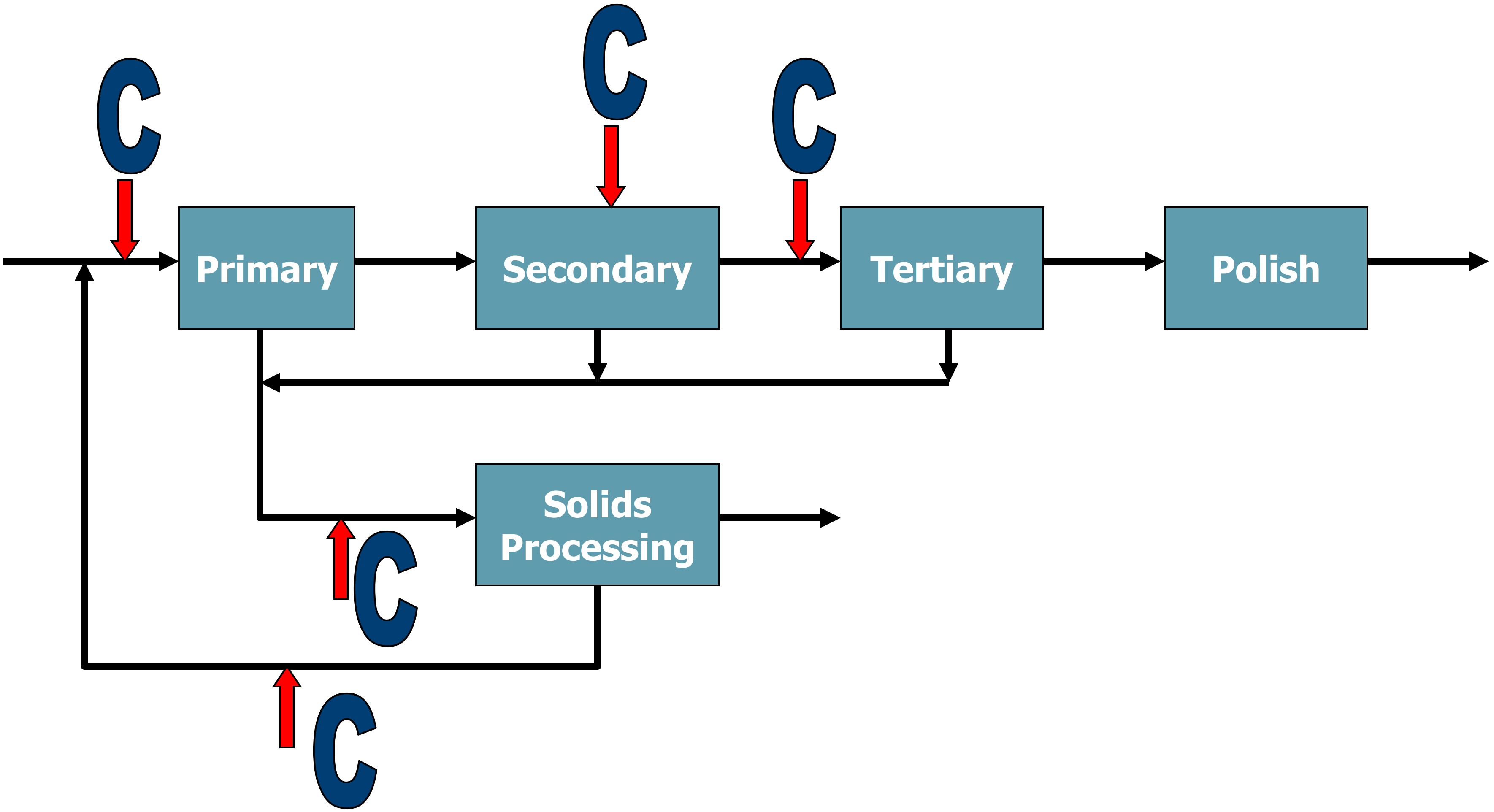
The exception



Convert to Particulate



Typical Chemical Treatment Opportunities



Chemicals used for Phosphorus Precipitation

Chemical	***Formula***	***Removal mechanism***	***Effect on pH***
Aluminum Sulfate (Alum)	$Al_2(SO4)_3.14.3(H_2O)$ M.W. = 599.4	Metal hydroxides	removes alkalinity
Ferric Chloride	$FeCl_3$ M.W. = 162.3	Metal hydroxides	removes alkalinity
Poly Aluminum Chloride	$Al_nCl_{(3n-m)}(OH)_m$ $Al_{12}Cl_{12}(OH)_{24}$	Metal hydroxides	none
Ferrous sulfate (pickle liquor)	Fe_2SO_4	Metal hydroxides	Removes alkalinity
Lime	CaO, $Ca(OH)_2$	Insoluble precipitate	Raises pH to above 10

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Ferric Reaction with Phosphorus

The following illustrates a "stoichiometric reaction" of Fe^{+++} with P

$$\mathbf{FeCl_3 + H_3PO_4 \;=\; FePO_4 + 3HCl_3}$$

1 mole of Fe reacts with 1 mole P

➔5.2 mg ferric per mg P
➔0.92 mg alkalinity per mg of ferric

Alum Reaction with Phosphorus

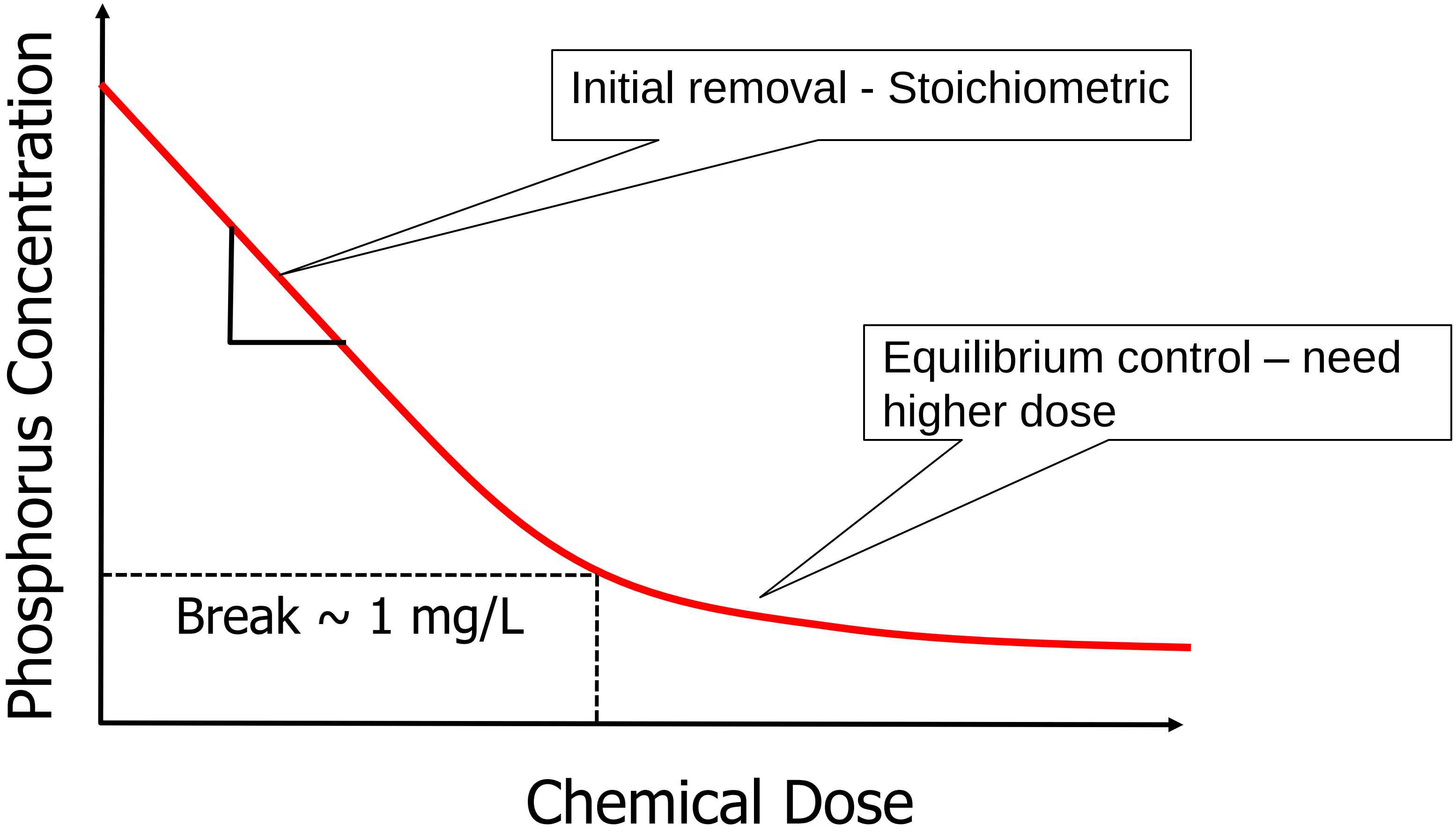
The following illustrates a "stoichiometric reaction" of Al^{+++} with P

$$\mathbf{Al_2(SO_4)_3 \cdot 14H_2O + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2SO_4 + 18H_2O}$$

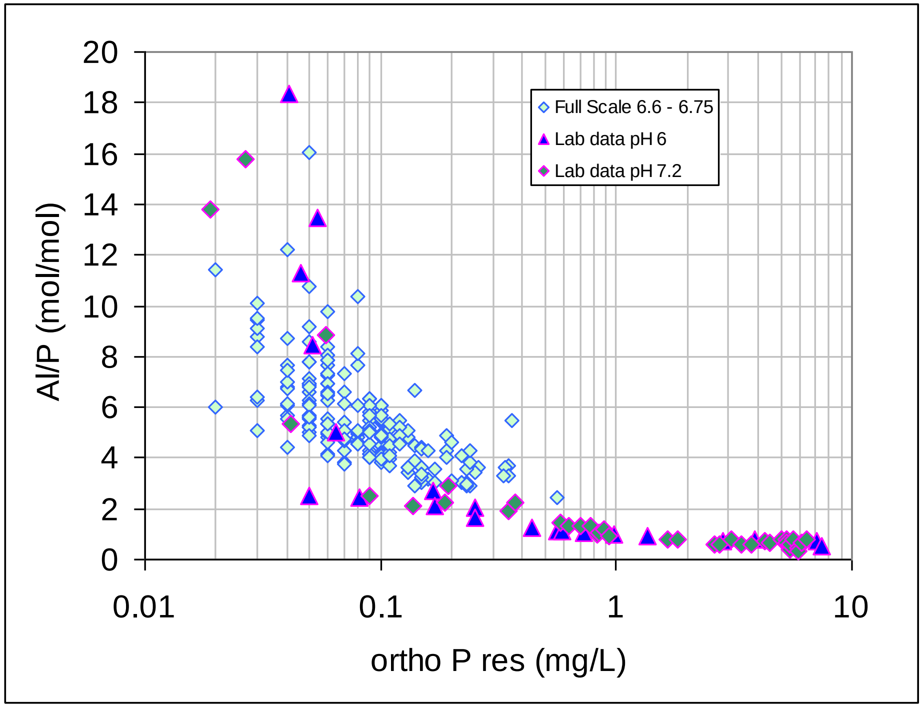
2 mole of Al reacts with 2 mole P (or 1 mole Al per mole P)

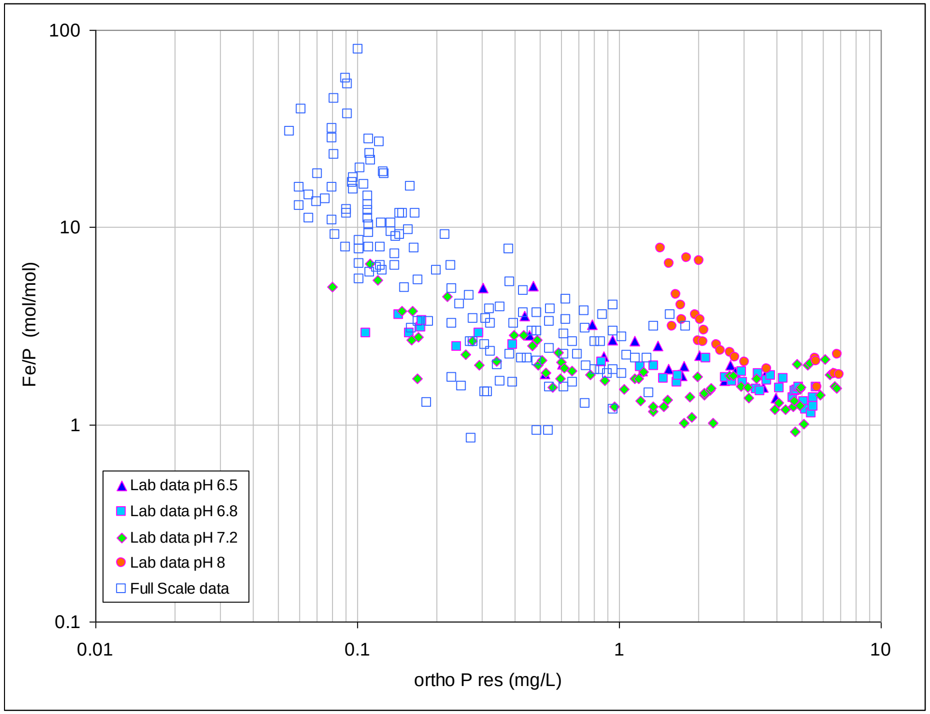
➔9.6 mg alum per mg P
➔0.5 mg alkalinity per mg of Alum

Phosphorus Removal



Molar Dose Ratio From Tests



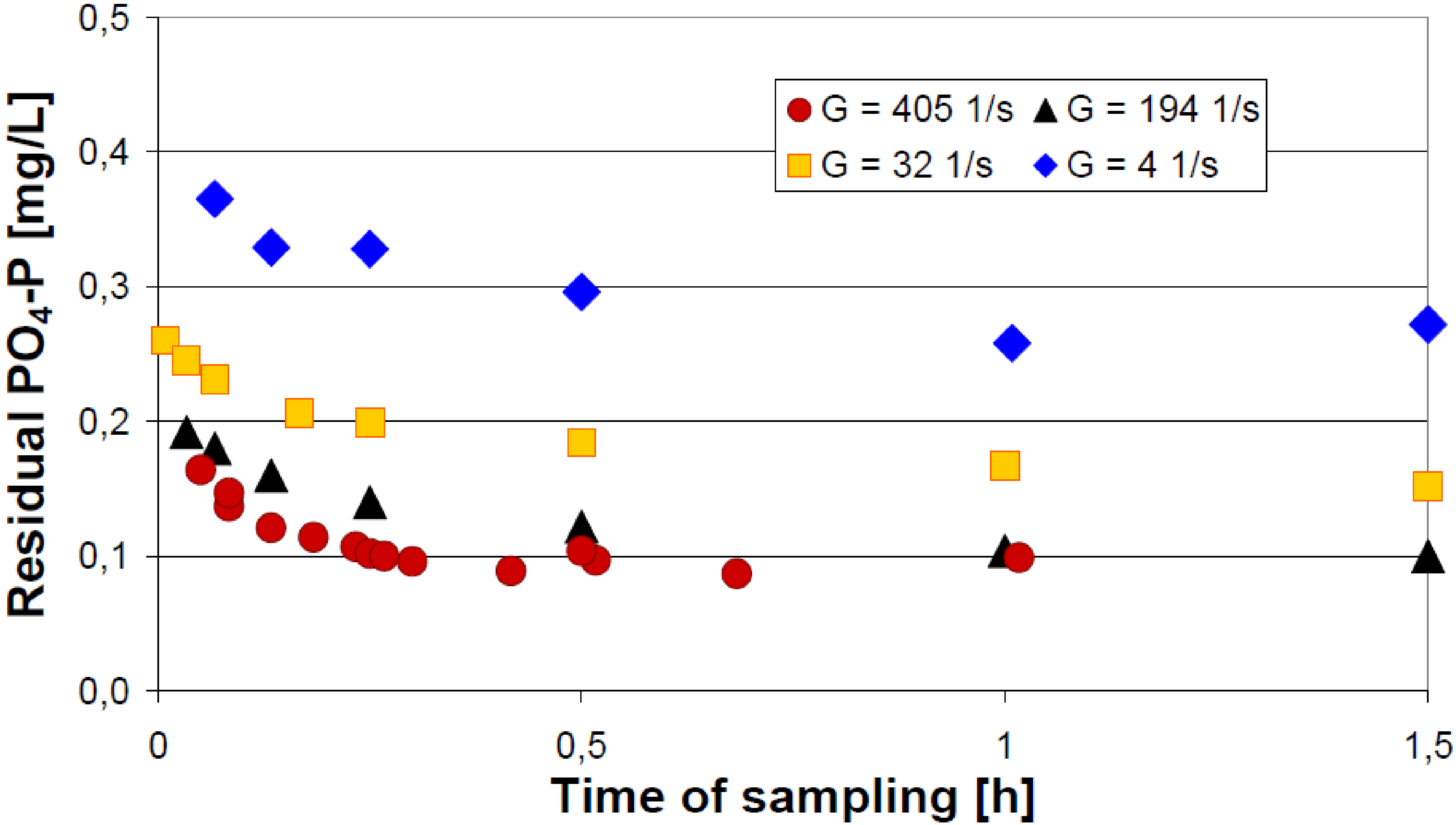


Slav Hermanowicz, Chemical Fundamentals of Phosphorus Precipitation, WERF Boundary Condition Workshop, Washington DC, 2006

Exact Molar Ratios Versus Effluent Soluble P will Vary with Applications

- 1.5 to 2.0 Molar ratios for 80-98 percent removal
- 5.0 to 7.0 Molar ratios for higher efficiency and to reach low minimal soluble P concentrations
- Ratios are higher with PAC
- Factors that influence ratios
  - pH
  - Mixing method
  - Wastewater characteristics
    - Colloids and solids effect P-metal hydroxide complexations
    - Organic subtrates
    - Iron and aluminum can react with humic substances

Kinetics and Mixing of Phosphorus / Alum Reaction



Szabó et al. (2006) The Importance Of Slow Kinetic Reactions In Simultaneous Chemical P Removal, WEFTEC 2006

Photomicrographs of Phosphate Precipitants

What is

REALLY

Forming?

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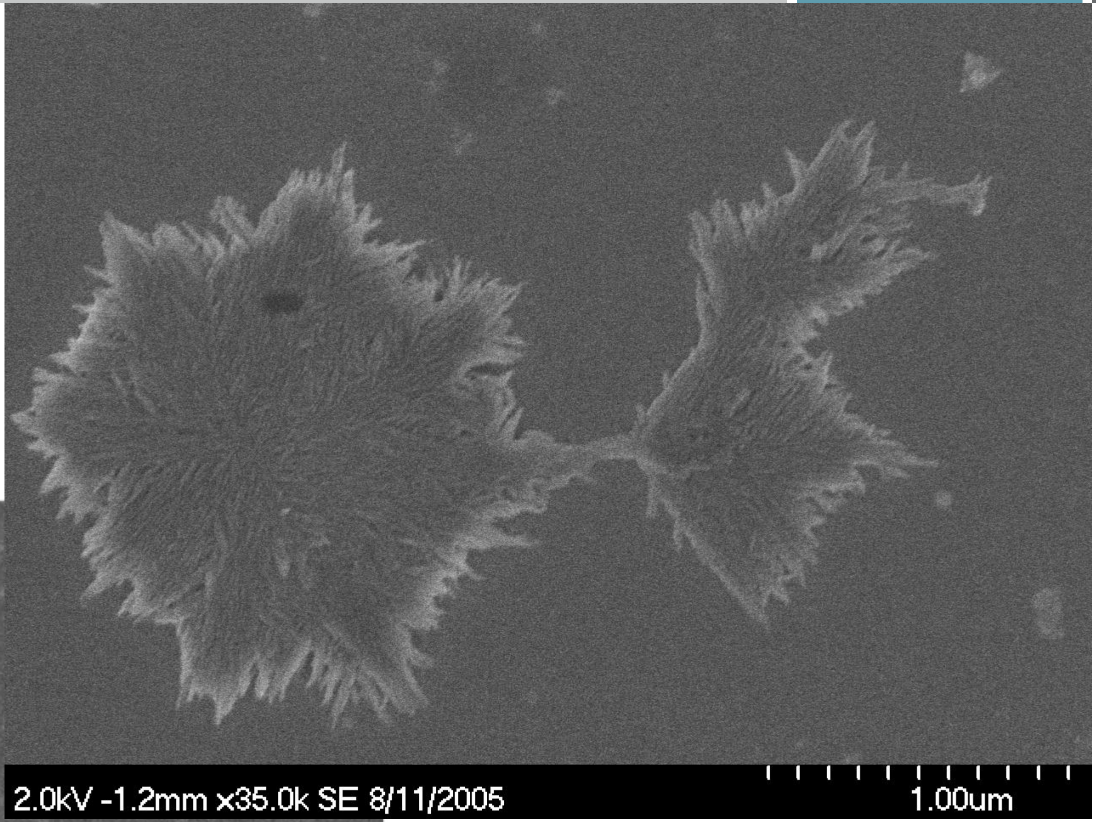
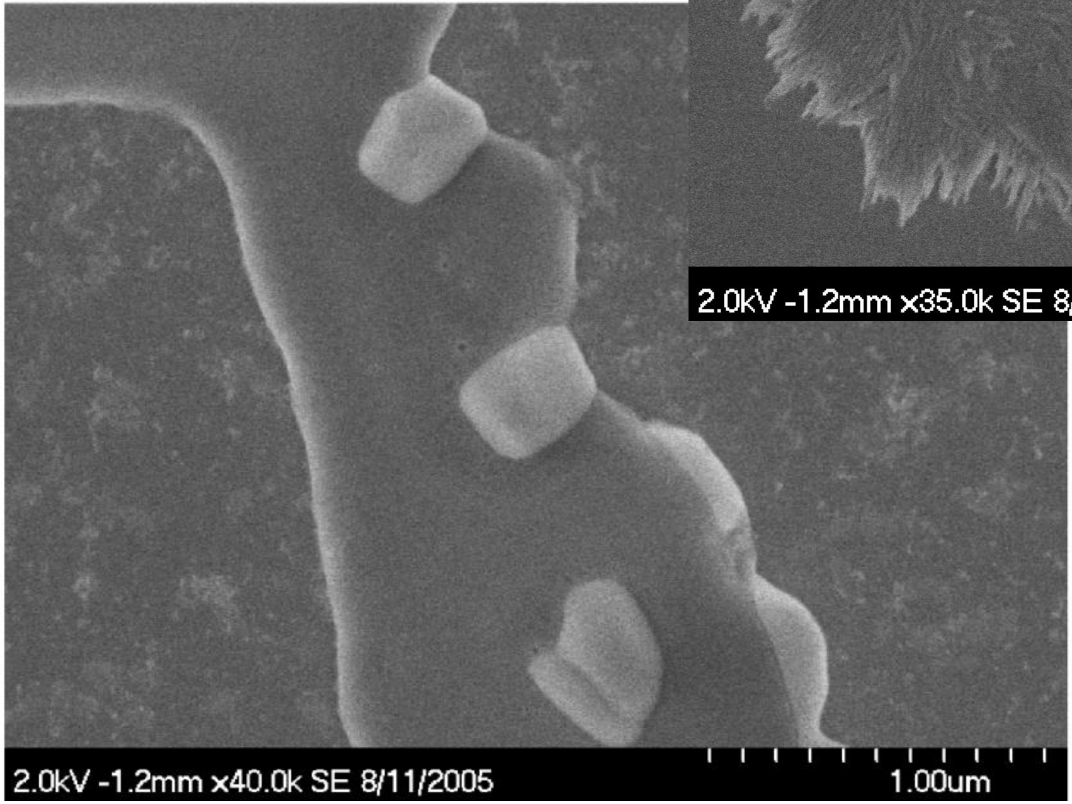
pH 7-->

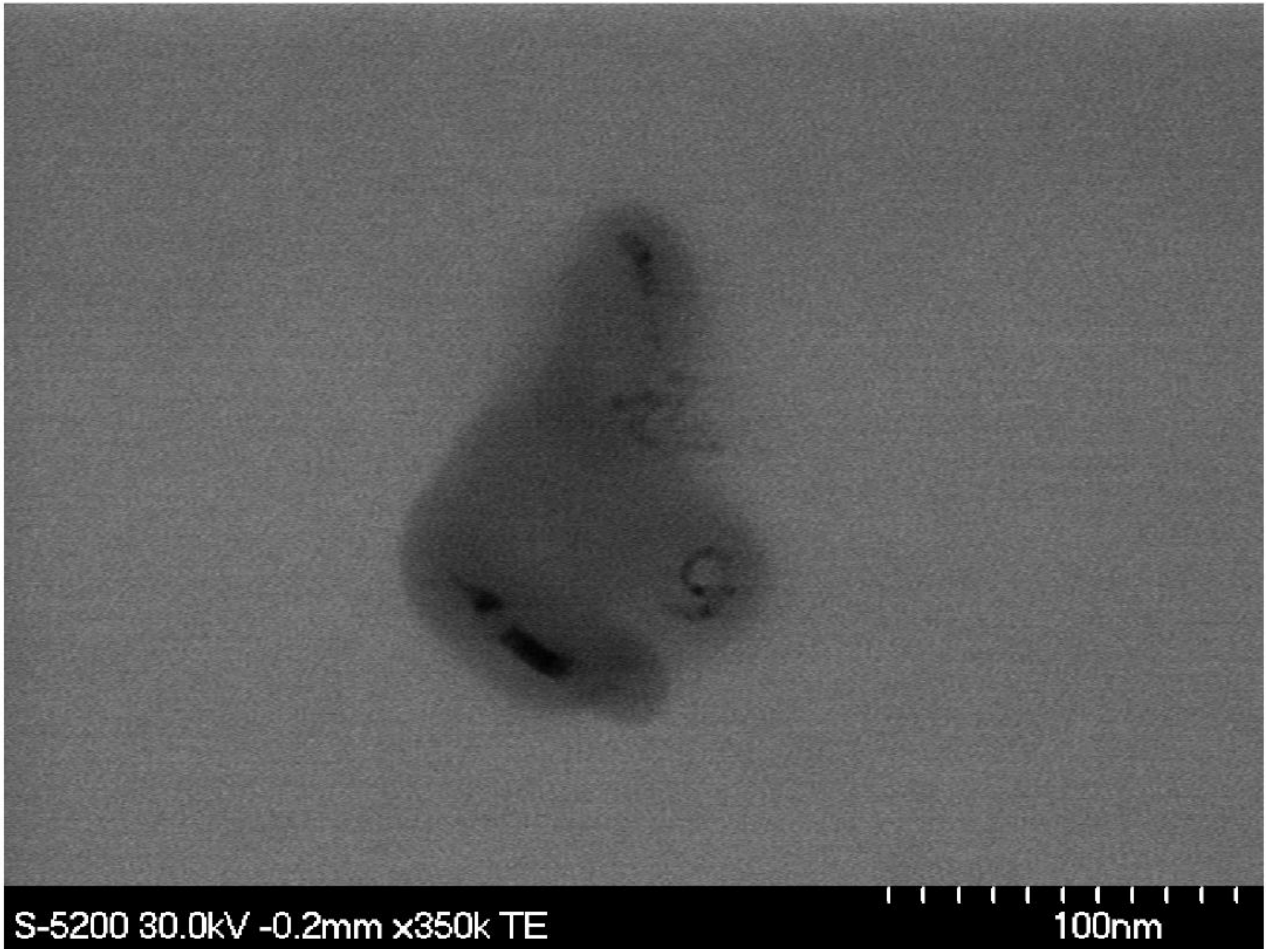




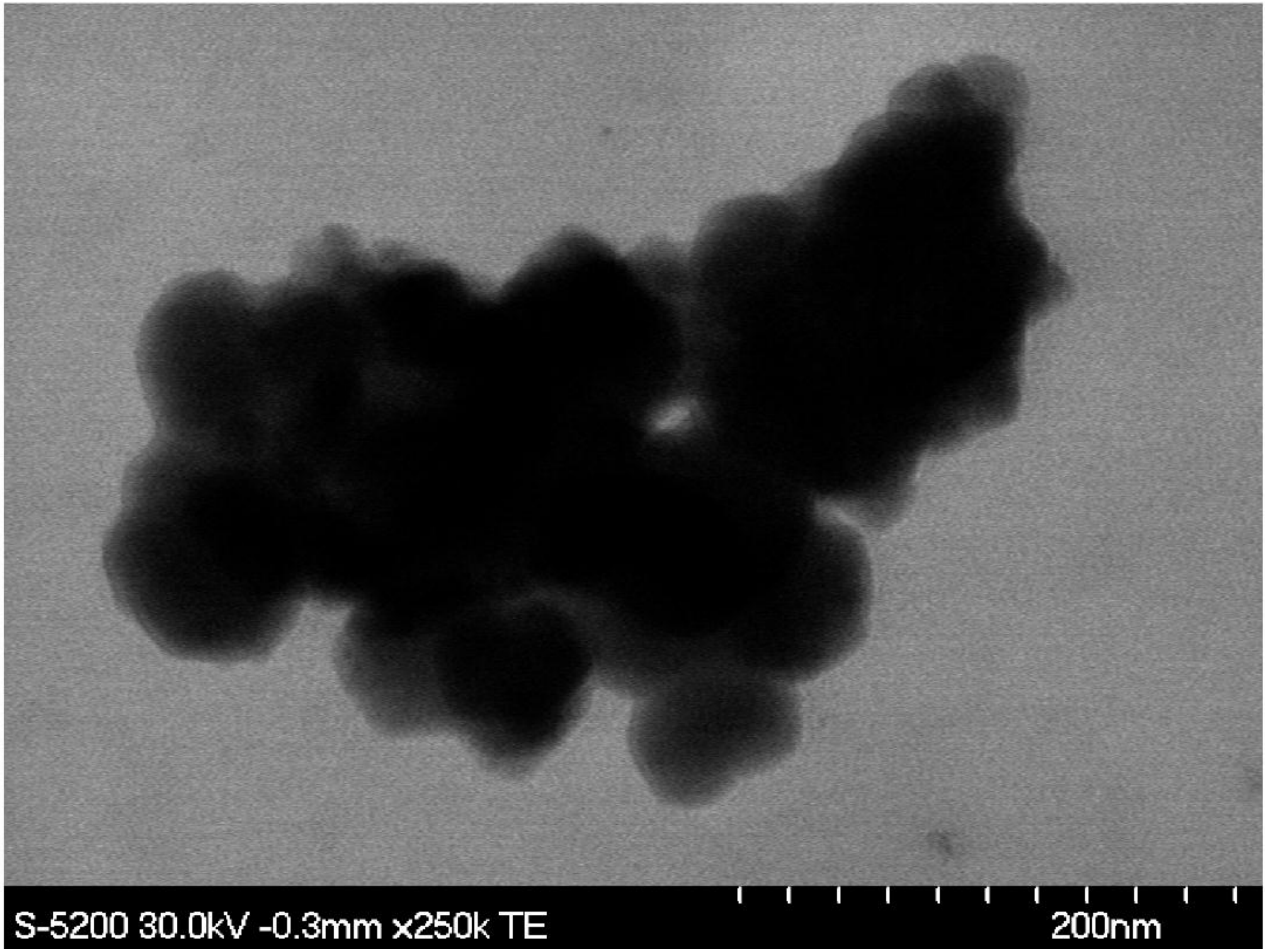
← pH 3

Scott Smith, Wilfrid Laurier University

Fresh HFO



Young HFO



$FePO_4$ precipitant

After 4 days.

Aged HFO

HFO precipitant

After 2 years.
Hard !!

Metal Hydroxide Removal of P Found for Ferric Addition

- Metal hydroxide formed
- Co precipitation of P into hydrous ferric oxides structure
  - $Fe(OH)_3$, $Fe(OH)_4^-$
- Surface complexation between P and metal hydroxide compounds
- Phosphorus and Iron share oxygen molecule:
- $FeOOH + HOPO_3 = FeOOPO_3 + H_2O$
- Hydroxide formation can be simply represented:
  - **$FeCl_3 + 3H_2O \Rightarrow Fe(OH)_3 + 3\ HCl$**
  - **$Al_2(SO_4)_3.14H_2O + 3\ H_2O \Rightarrow 2Al(OH)_{3(s)} + 3H_2SO_4$**

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Closer Look at the Chemical Species

Phosphorus Speciation and Removal in Advanced Wastewater Treatment

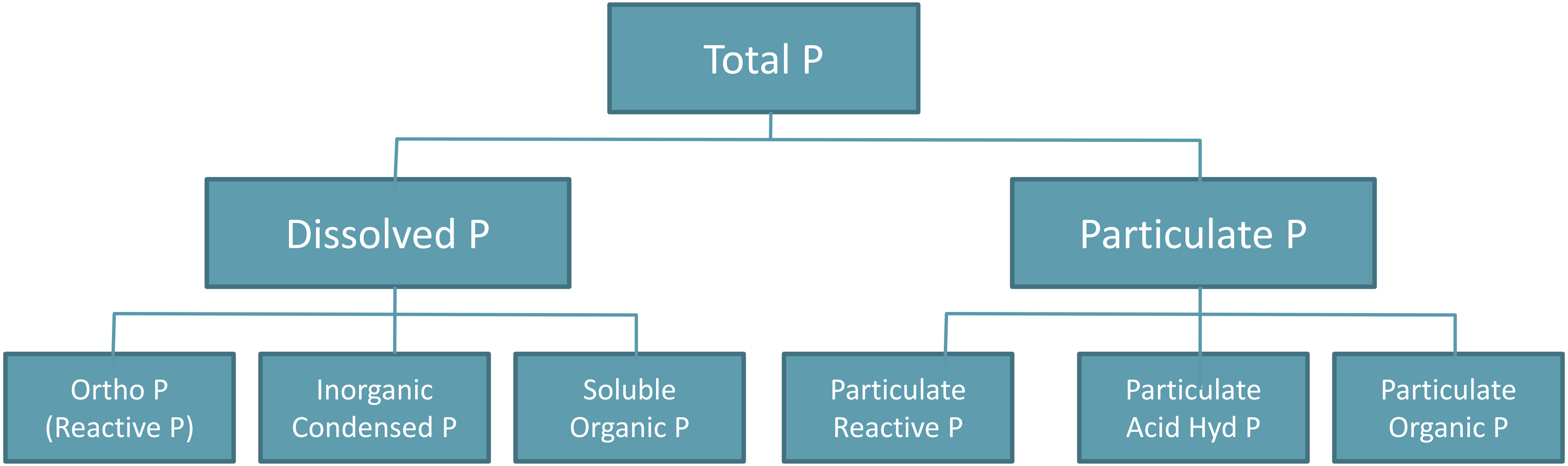
L. Liu, D. S. Smith, D. Houweling
J.B. Neethling, H.D. Stensel
S. Murthy, Amit Pramanik and A. Z. Gu

WERF

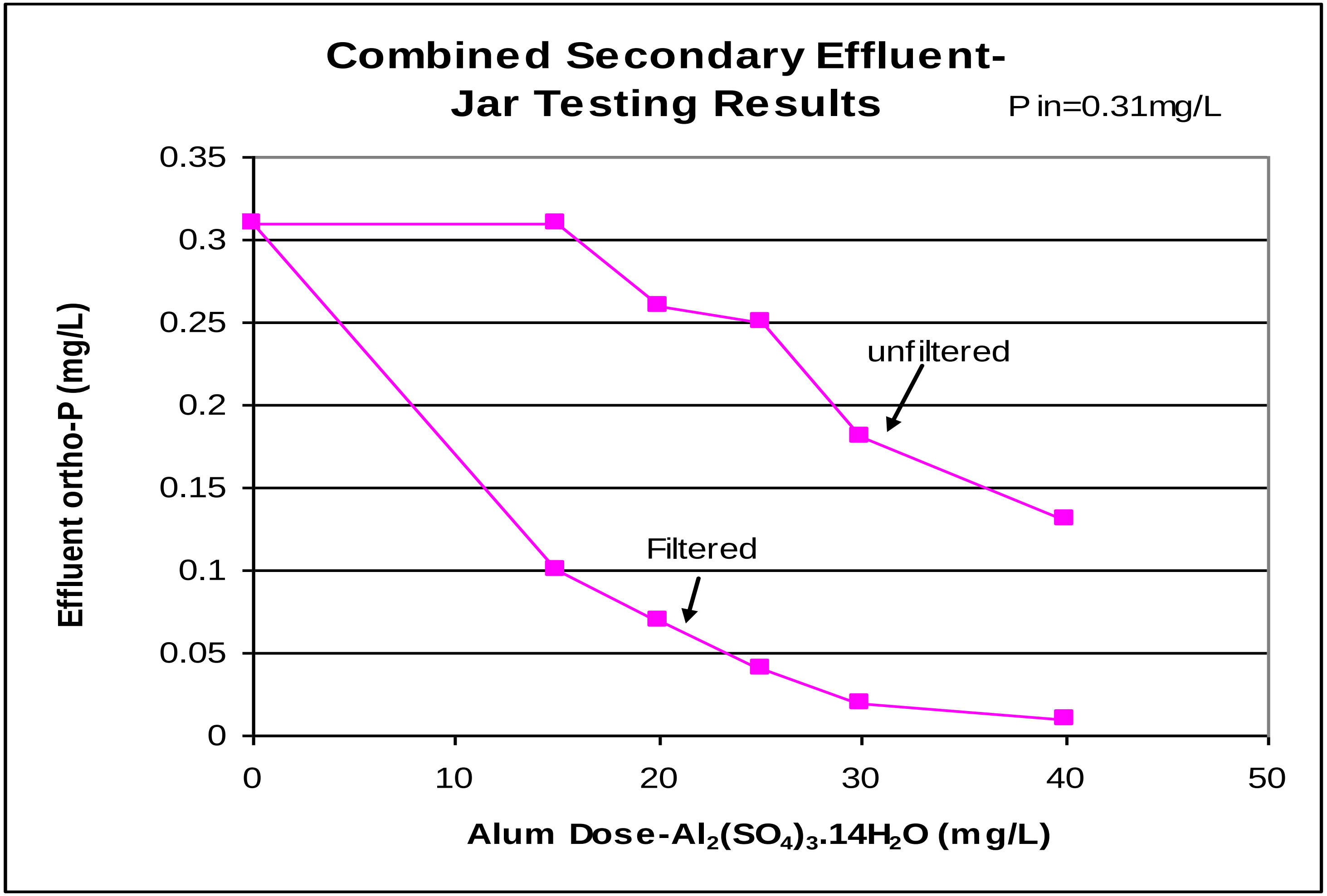
Analytical Definitions of Phosphorus Species

- Filterable/nonfilterable (soluble?)
  - Passing through filter paper
  - Could be colloidal (very small particles)
- Reactivity to analytical procedure
  - Measure for orthophosphate
- Pretreatment (acid hydrylosis, digestion, etc)
  - Convert larger molecules to be reactive (orthophosphate)

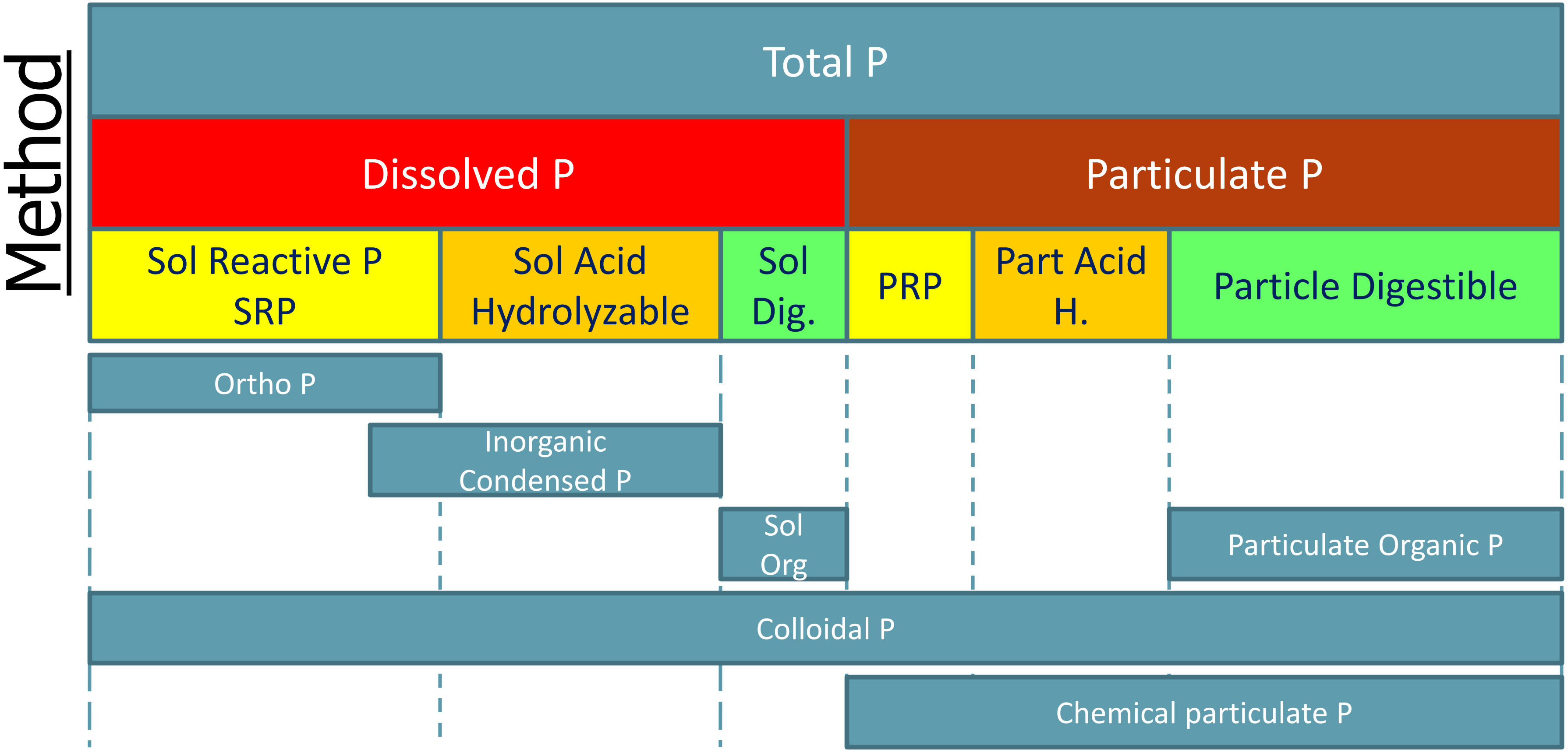
Phosphorus Species Categories



Particulate Chemical Precipitant Measures as Reactive P



Analytical Definition Based Phosphorus Fractions/Species



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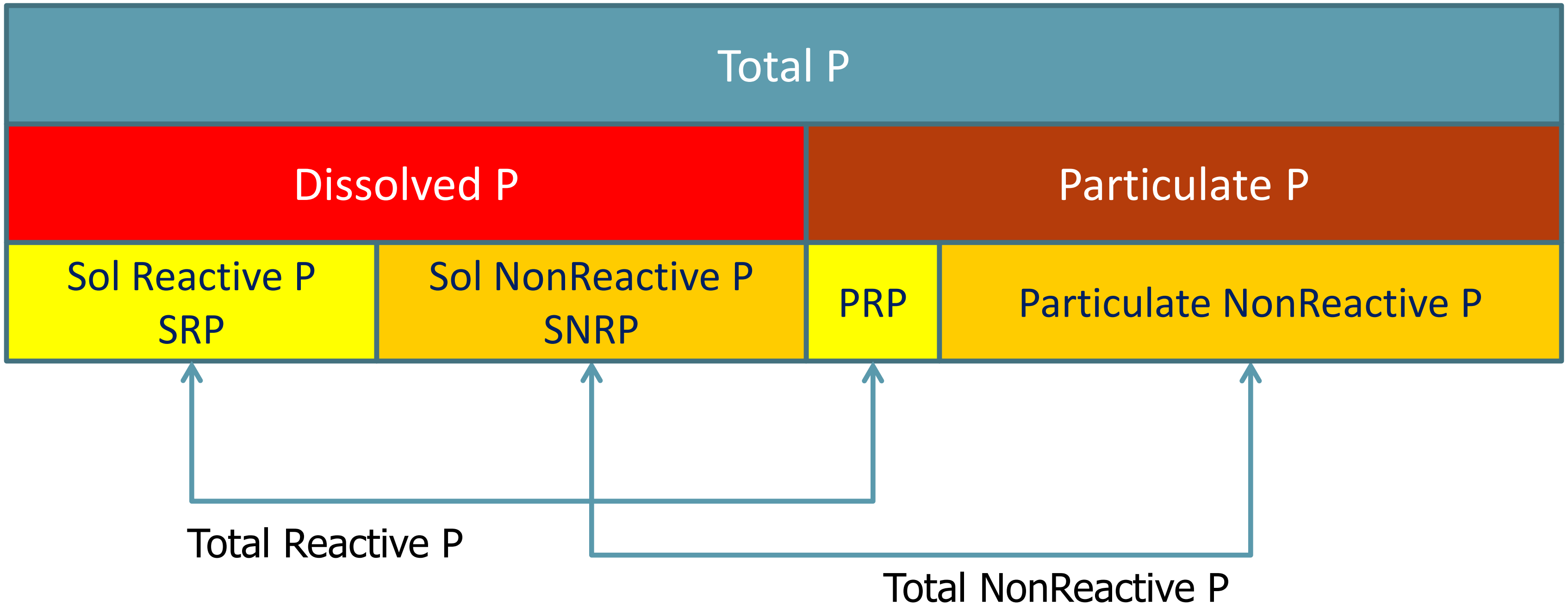
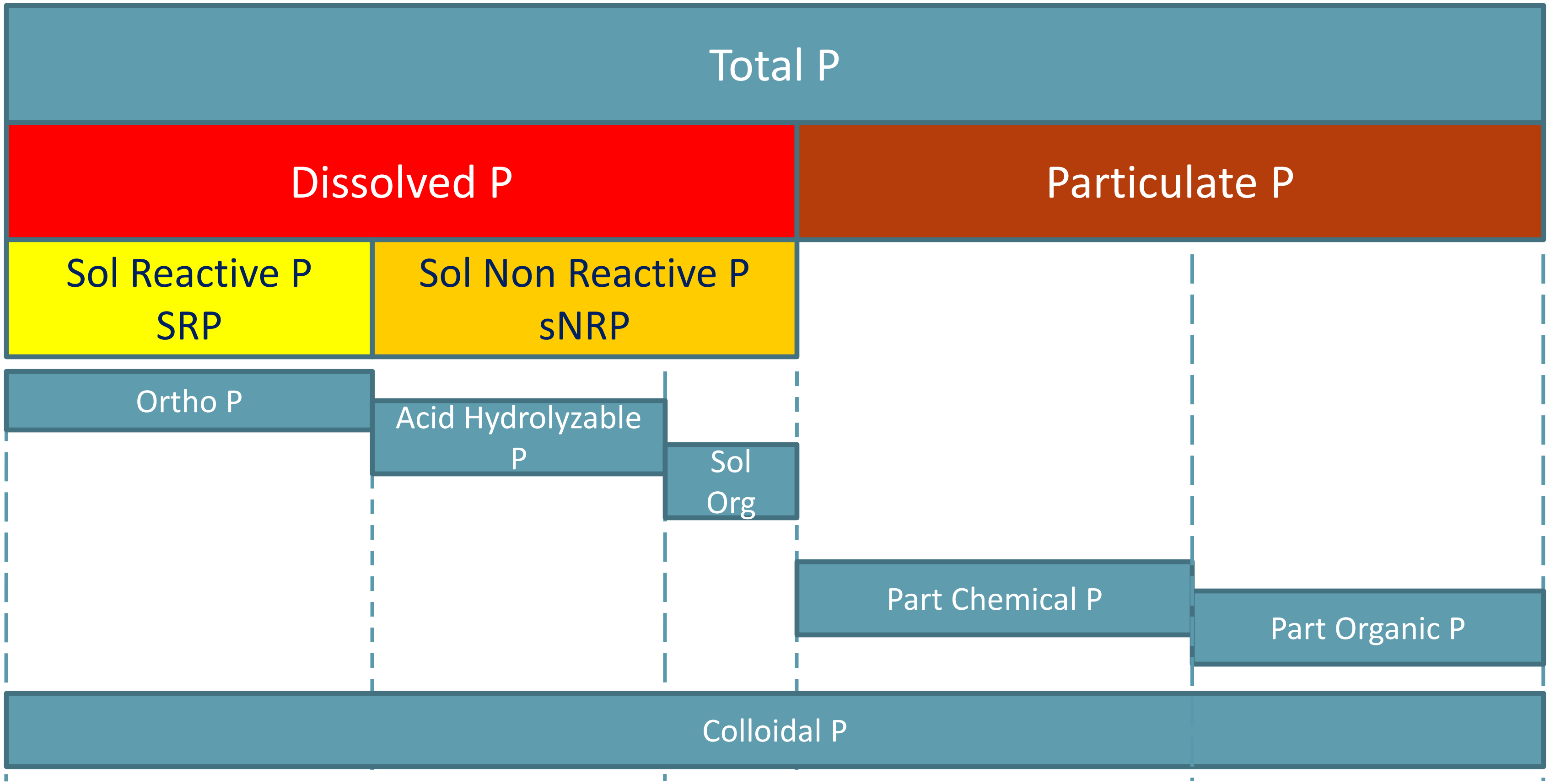
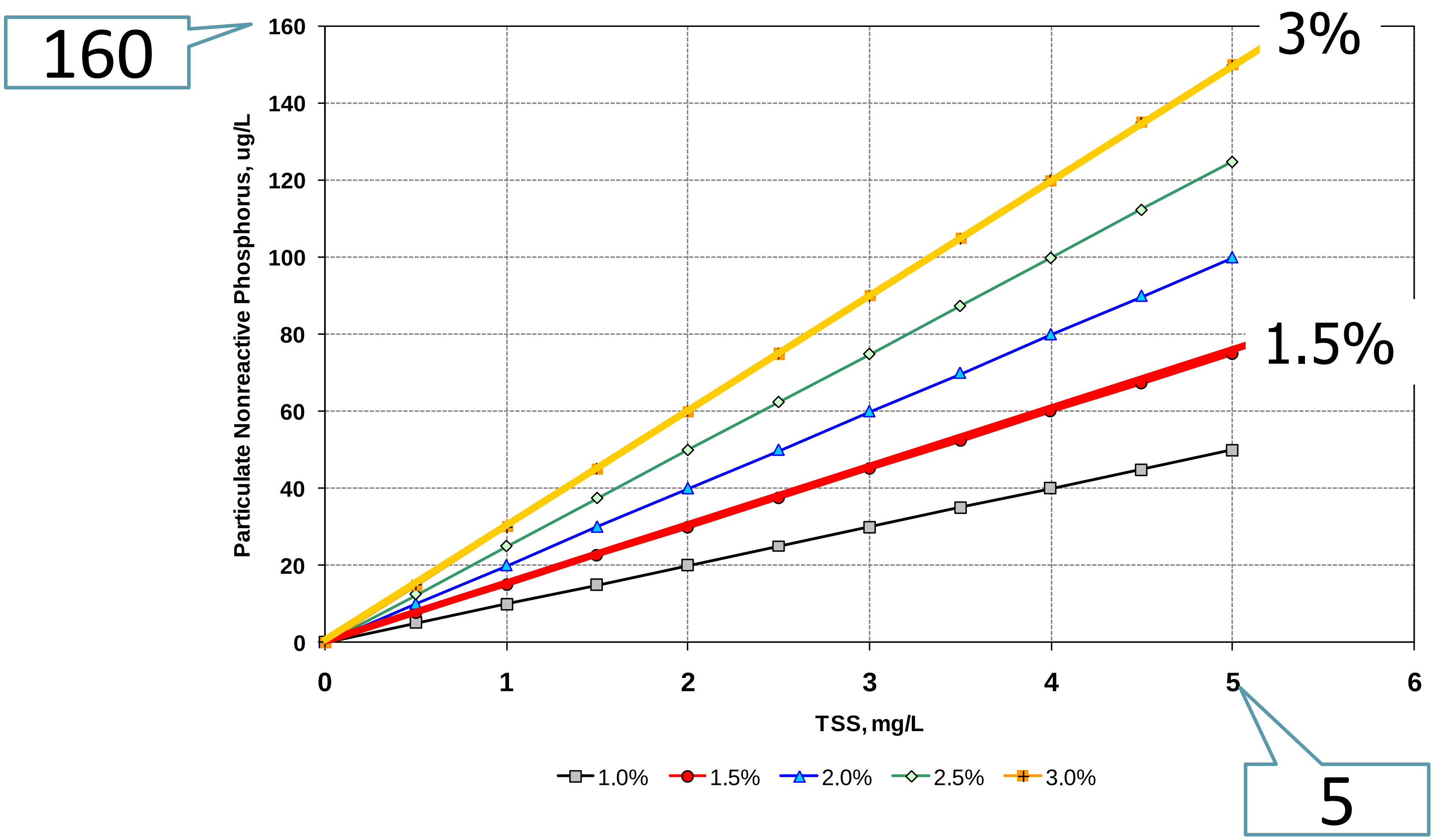
Nonreactive Phosphorus



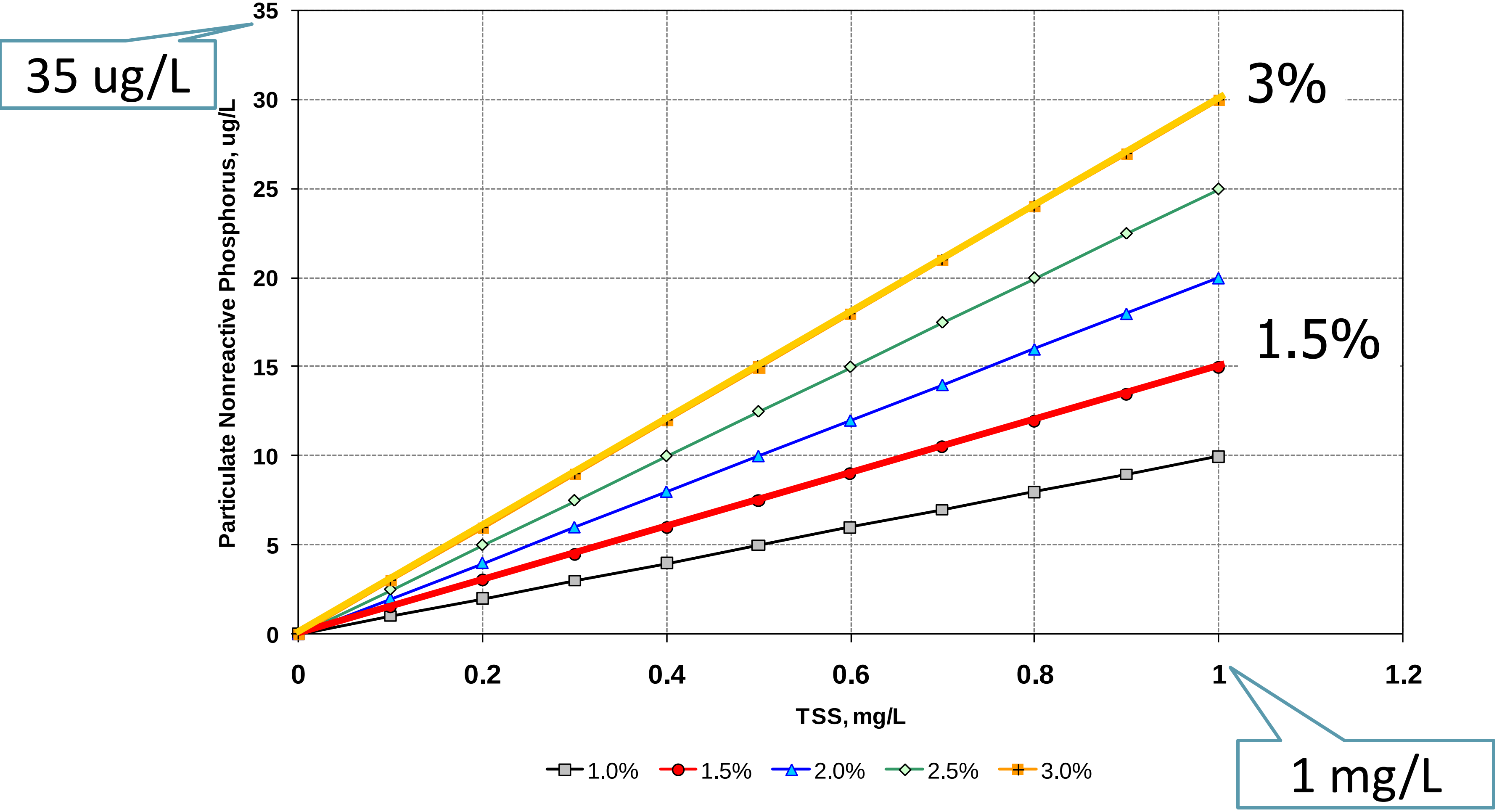
Analytical Definition Based Phosphorus Fractions/Species



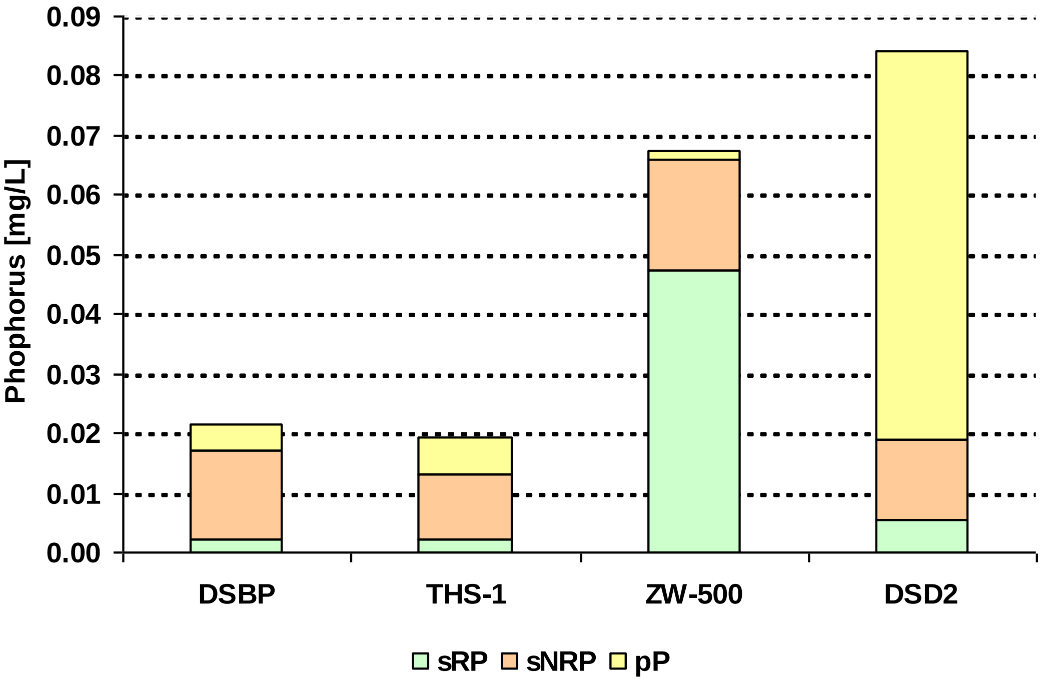
Secondary Effluent TSS adds to Particulate NRP



Filtered Effluent TSS adds to Particulate NRP



Pilot Study Results Illustrated Challenges at Limits of Technology



- No Treatment Technology Available for SNRP
- Portion May Not Be Bioavailable / Biodegradable

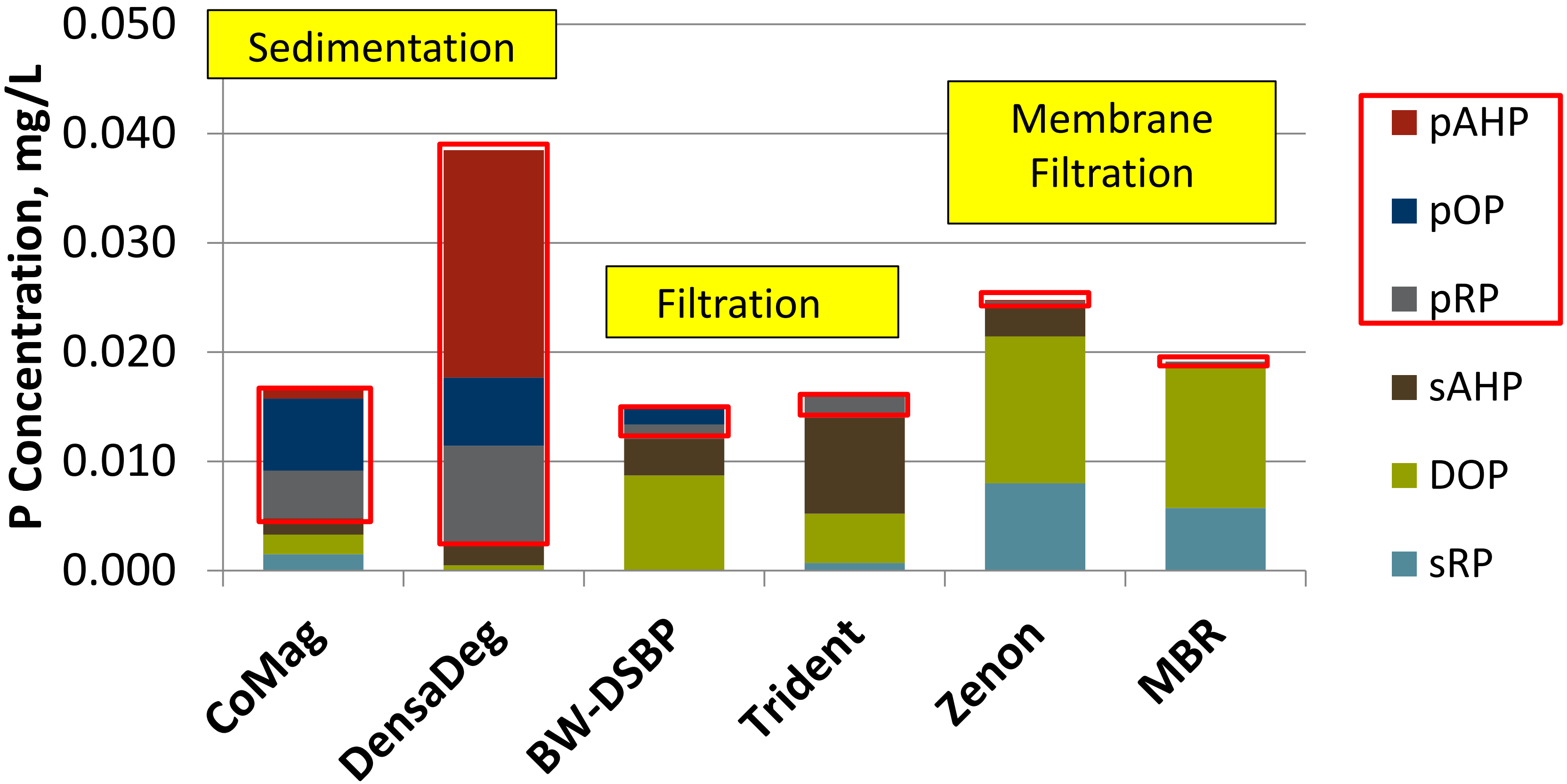
Particulate P

Soluble NonReactive P

Soluble Reactive P

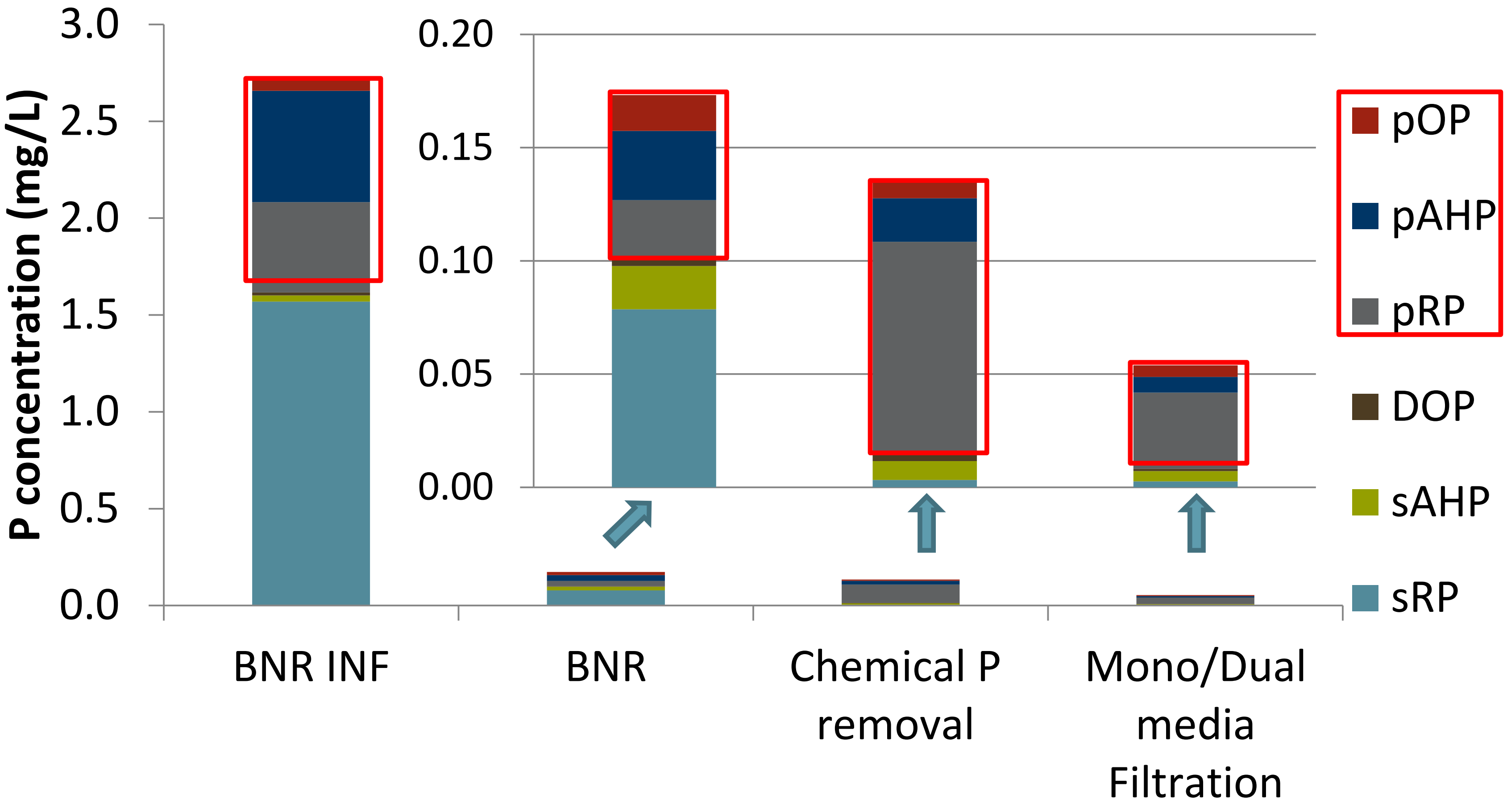
Neethling et al, 2007

Effluent P Fractions From Advanced Tertiary Treatment Processes



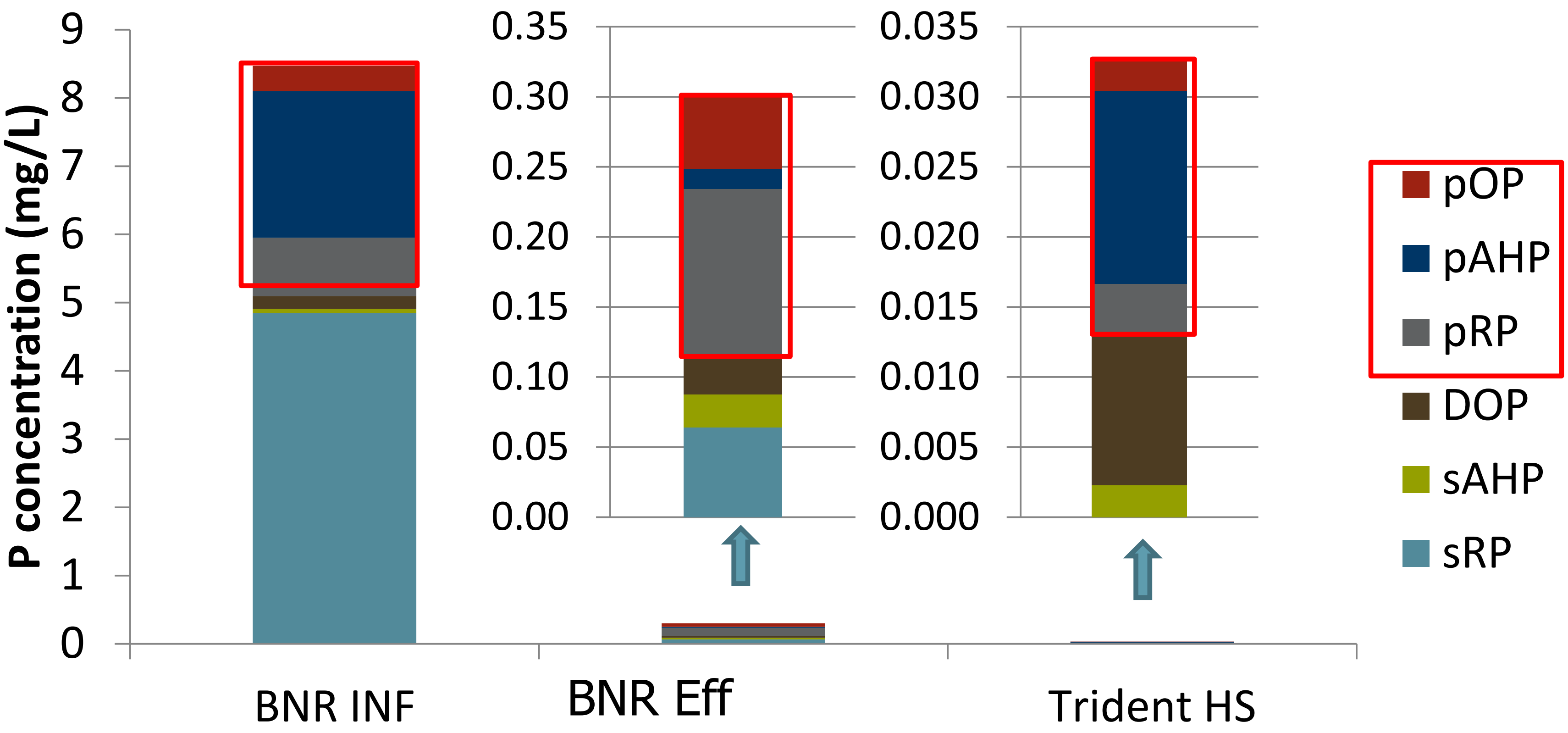
Lui, Gu, et al. (ongoing) Phosphorus Speciation and Removal in Advanced Wastewater Treatment, WERF Report

P fractions at Plant N



- sAHP seems to remain after BNR, associated with biomolecules
- Chemical addition converts sRP into pRP
- Chemical sRP (PO_4) removal relies pRP removal

Comparison of P fractions at Plant P



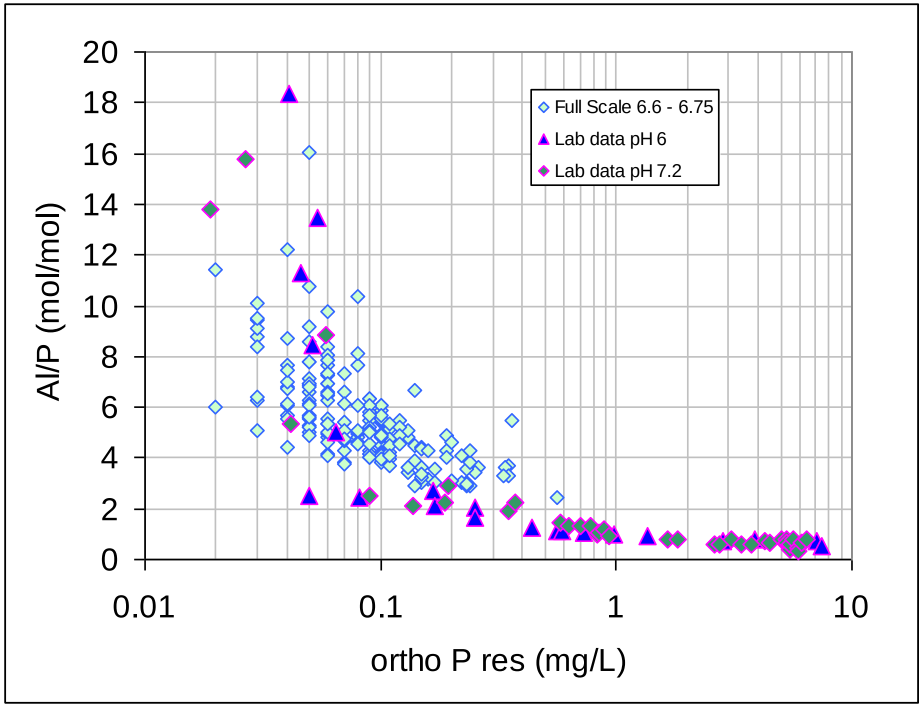
- Plant P and N are similar as (BNR+sedimentation +Filtration): composition very different
- DOP dominant soluble fraction; pAHP major particulate form
- Multi stage barrier remove TP to lower level

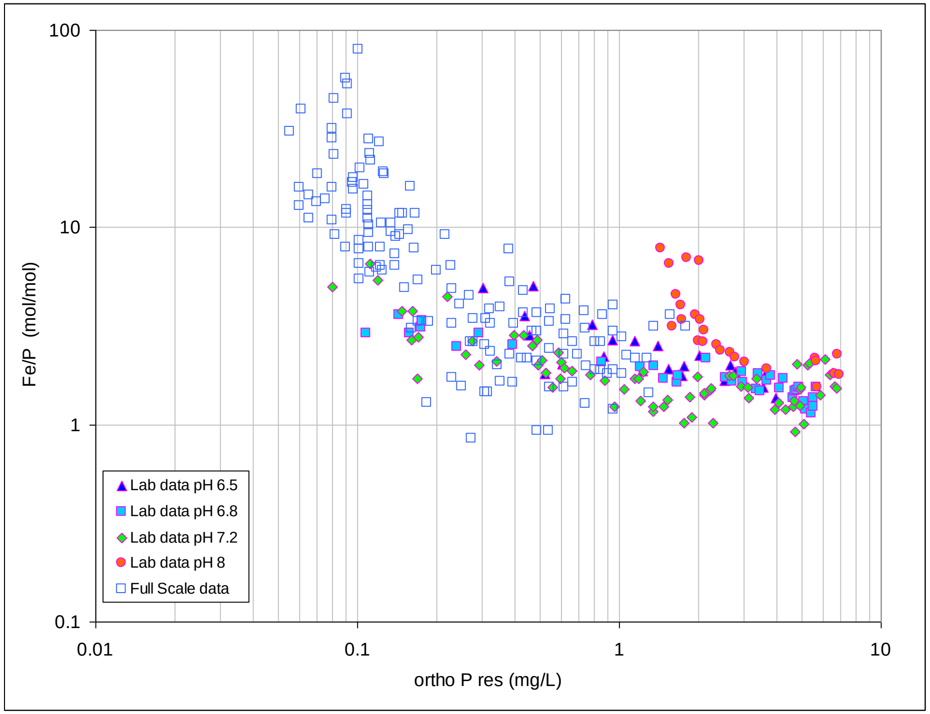
Opportunities for Optimization

Opportunities for Improvement

- Improve understanding of chemical kinetics
  - Dose relationships
  - Reuse formed metal hydroxides
- Enhance solids separation

Molar Dose Ratio From Tests





Single Step Chemical Addition Requires High Dose

		One Step
P entering	mg/L	5
P residual	mg/L	0.1
Alum/P dose	mol/mol	5
Alum/P dose	mg/mg	48
Alum dose	mg/L	235

Two Step Chemical Addition Reduce Dose

		One Step	Step 1	Step 2	Two Steps
P entering	mg/L	5	5	1	5
P residual	mg/L	0.1	1	0.1	0.1
Alum/P dose	mol/mol	5	1.5	5	2.1
Alum/P dose	mg/mg	48	14	48	21
Alum dose	mg/L	235	58	43	101

Two Step Chemical Addition Reduce Dose

		One Step	Step 1	Step 2	Two Steps
P entering	mg/L	5	5	1	5
P residual	mg/L	0.1	1	0.1	0.1
Alum/P dose	mol/mol	5	1.5	5	2.1
Alum/P dose	mg/mg	48	14	48	21
Alum dose	mg/L	235	58	43	101

Reuse Chemical Sludge to Reduce Dose and Increase Reliability

- Return chemical sludge to upstream process
- Build solids inventory – operate in solids contact mode

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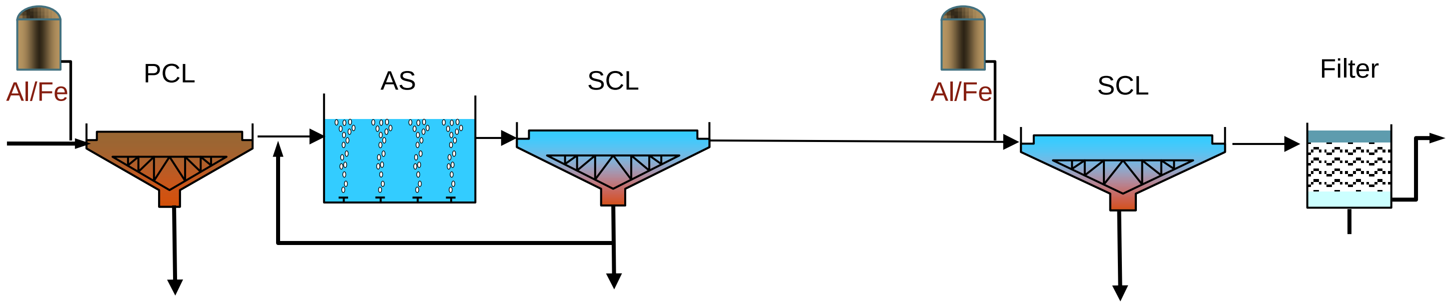
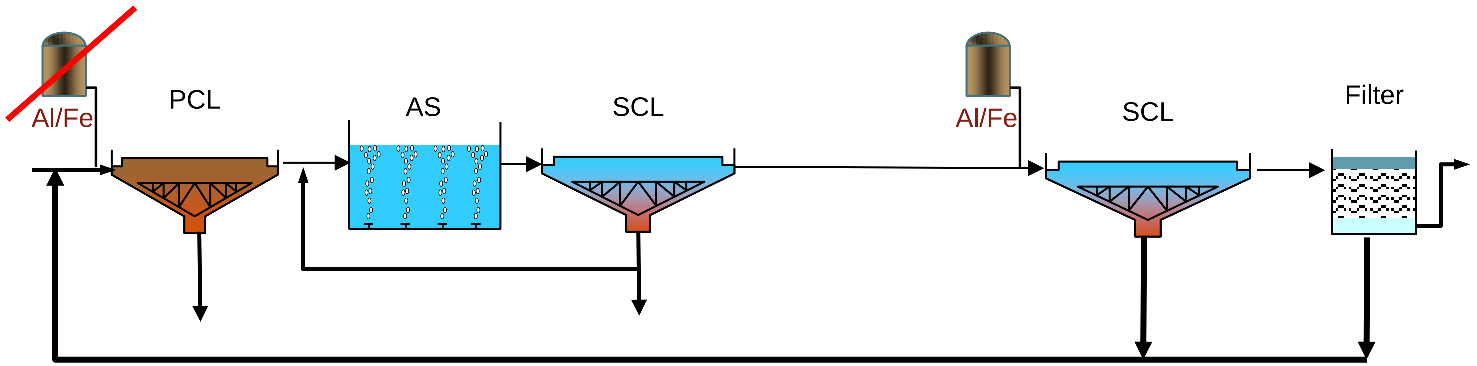
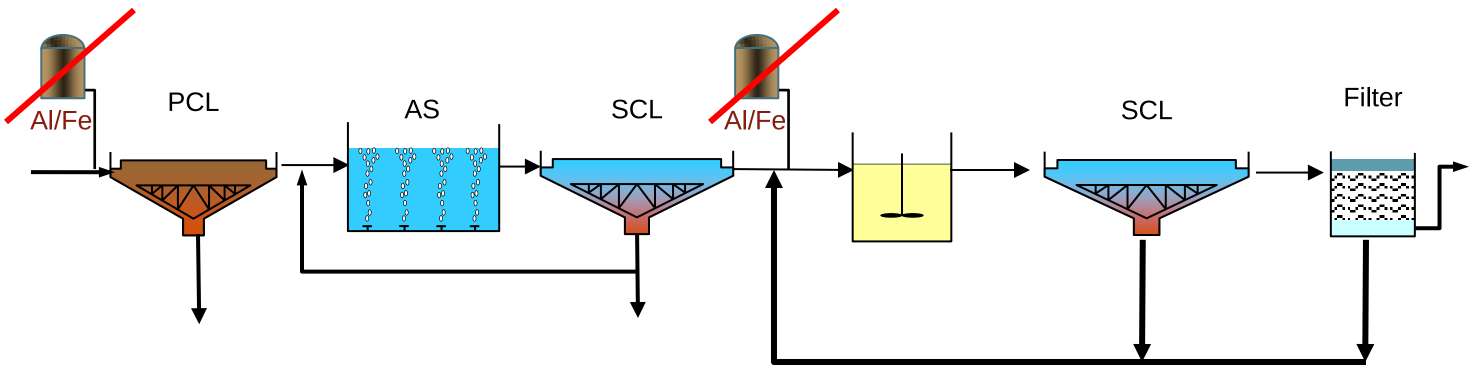
Conventional Tertiary Chemical P Removal



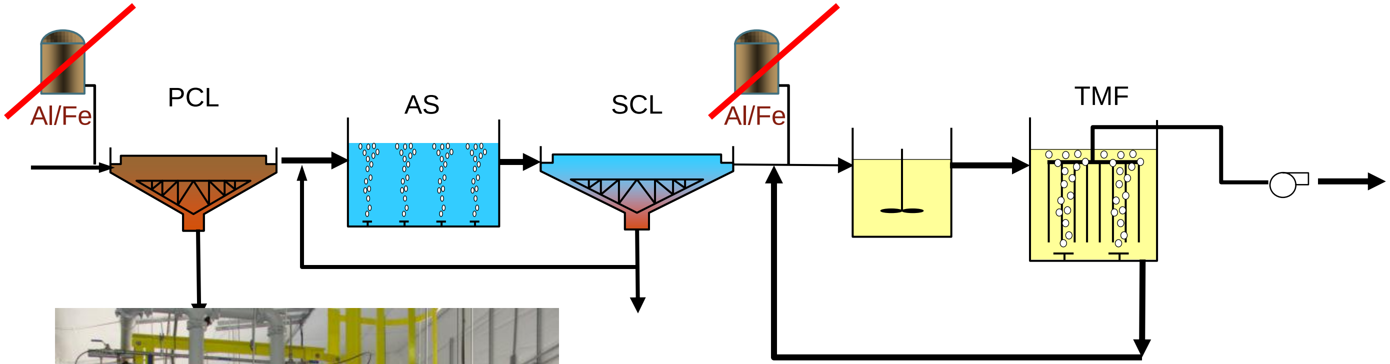
“ReUse” Chemical Sludge Upstream



Contact Clarification in Tertiary

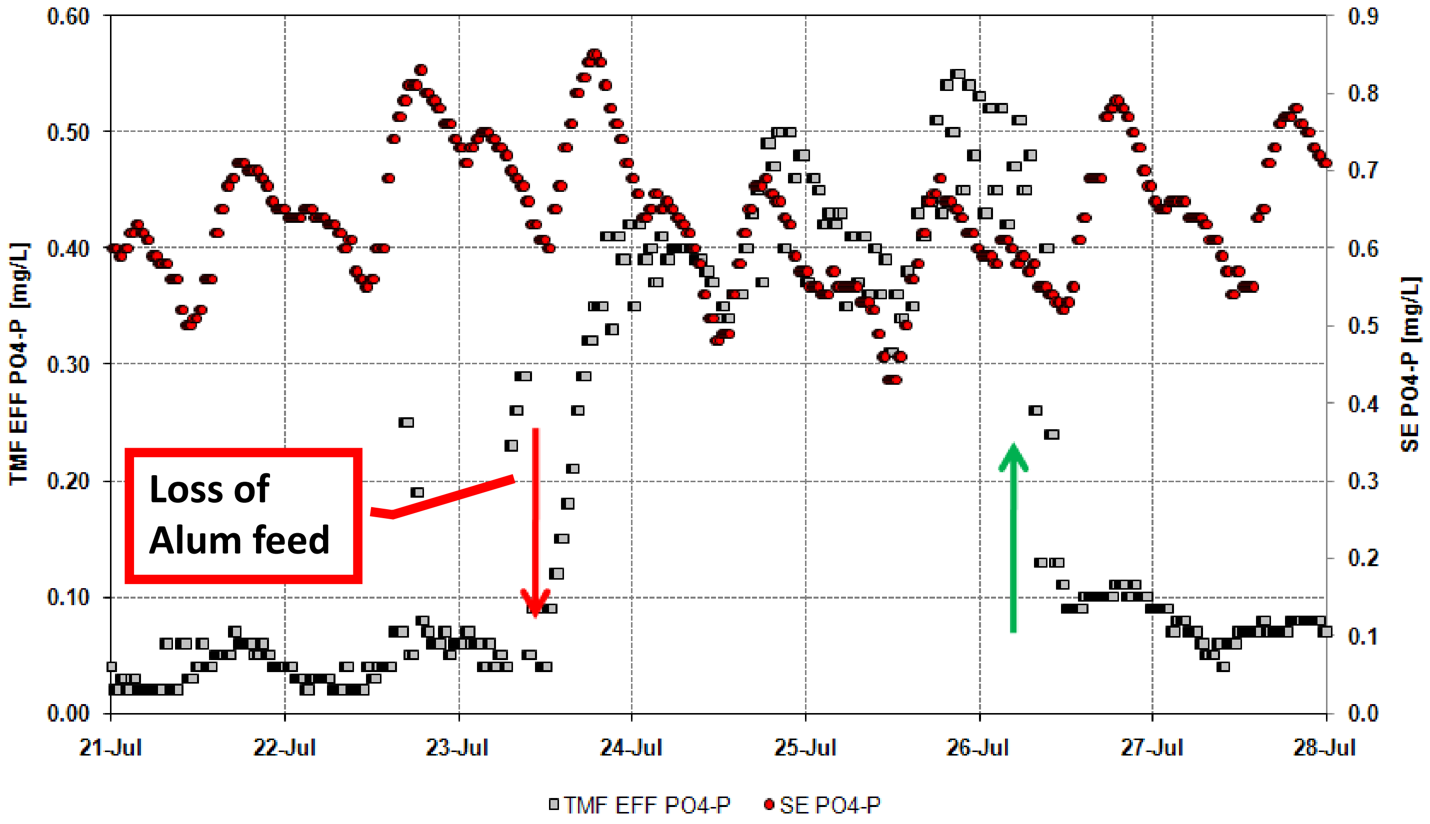


Coeur d’Alene: Microfiltration and Solids Recycle



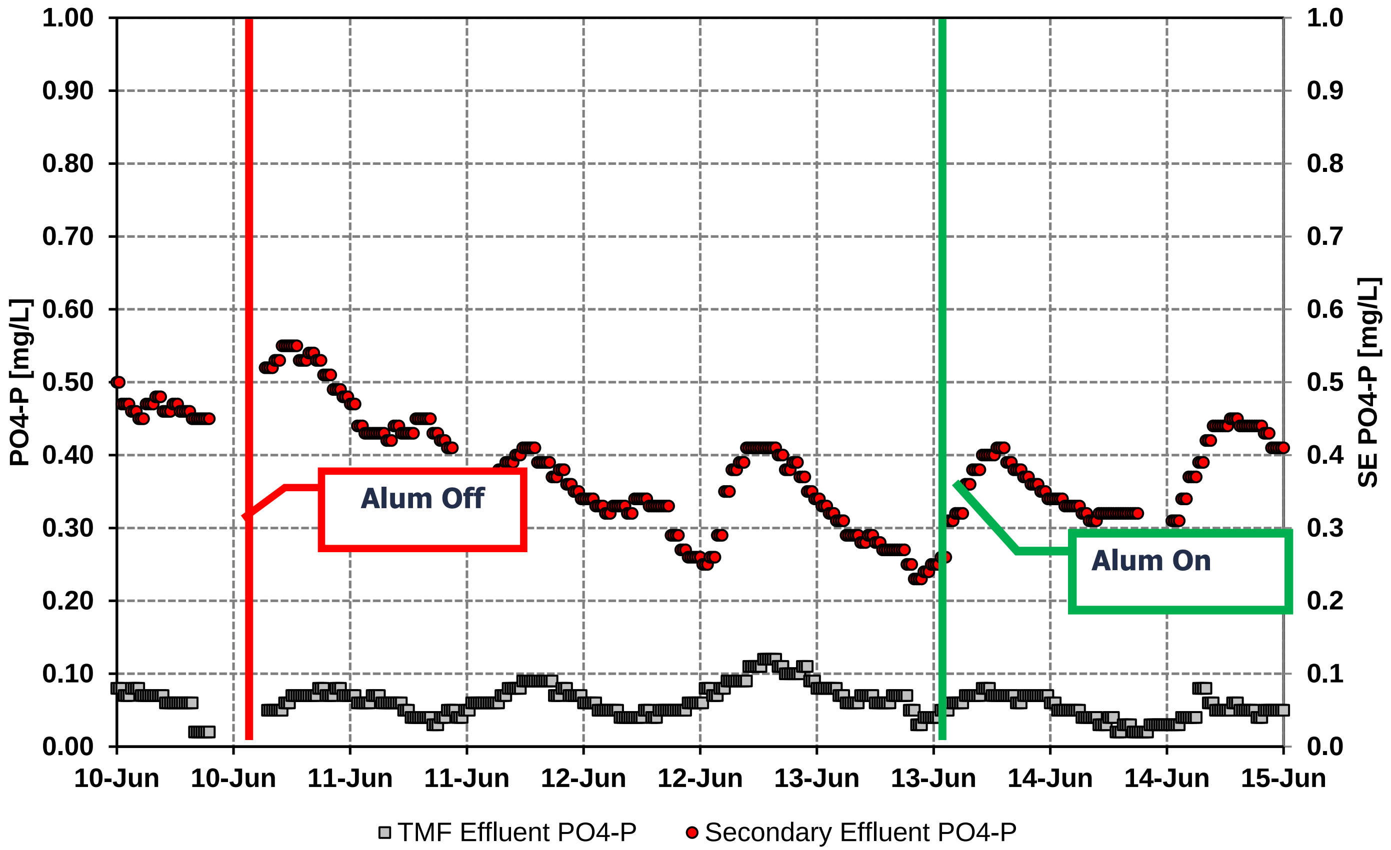
Implications for Design and Operation – Coeur d'Alene Pilot

No Solids Inventory



Implications for Design and Operation – Coeur d'Alene Pilot

With Solids Inventory



Summary and Conclusion - I

- Chemical reactions for phosphorus removal with ferric or alum is a primarily a surface complexation reaction
- Good mixing and contact time is needed to maximize chemical efficiency
- Preformed Metal Hydroxides retain the ability to react and remove phosphate

Summary and Conclusion - II

- Target phosphorus species for effective removal:
  - Precipitate Reactive Phosphorus – Phosphate
    - Increased dose can improve removal
  - Filter particulate fractions
    - High efficiency filters
  - Soluble Non-Reactive P remains difficult to remove
- Reuse metal hydroxides to reduce chemical use

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