Chemicals & Oxides

Rare Earth Technology in Wastewater Treatment

NEWEA Spring Meeting

June 3, 2019

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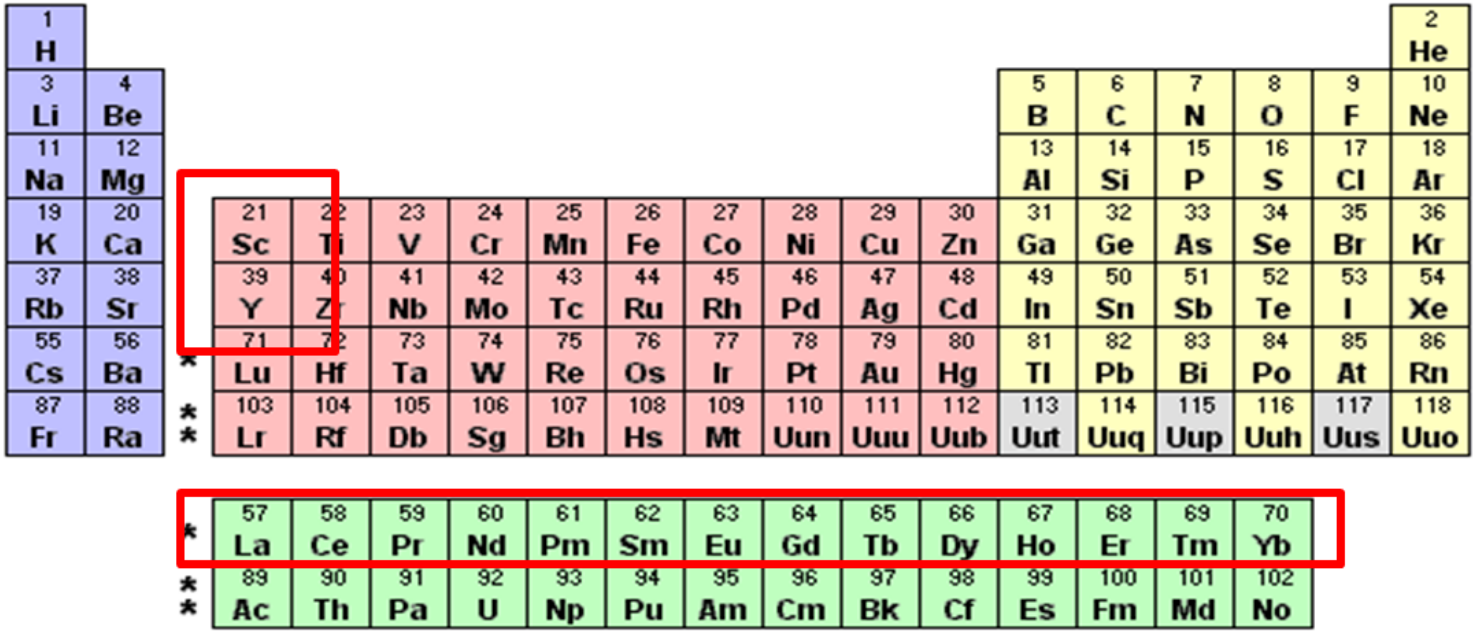
Session Overview

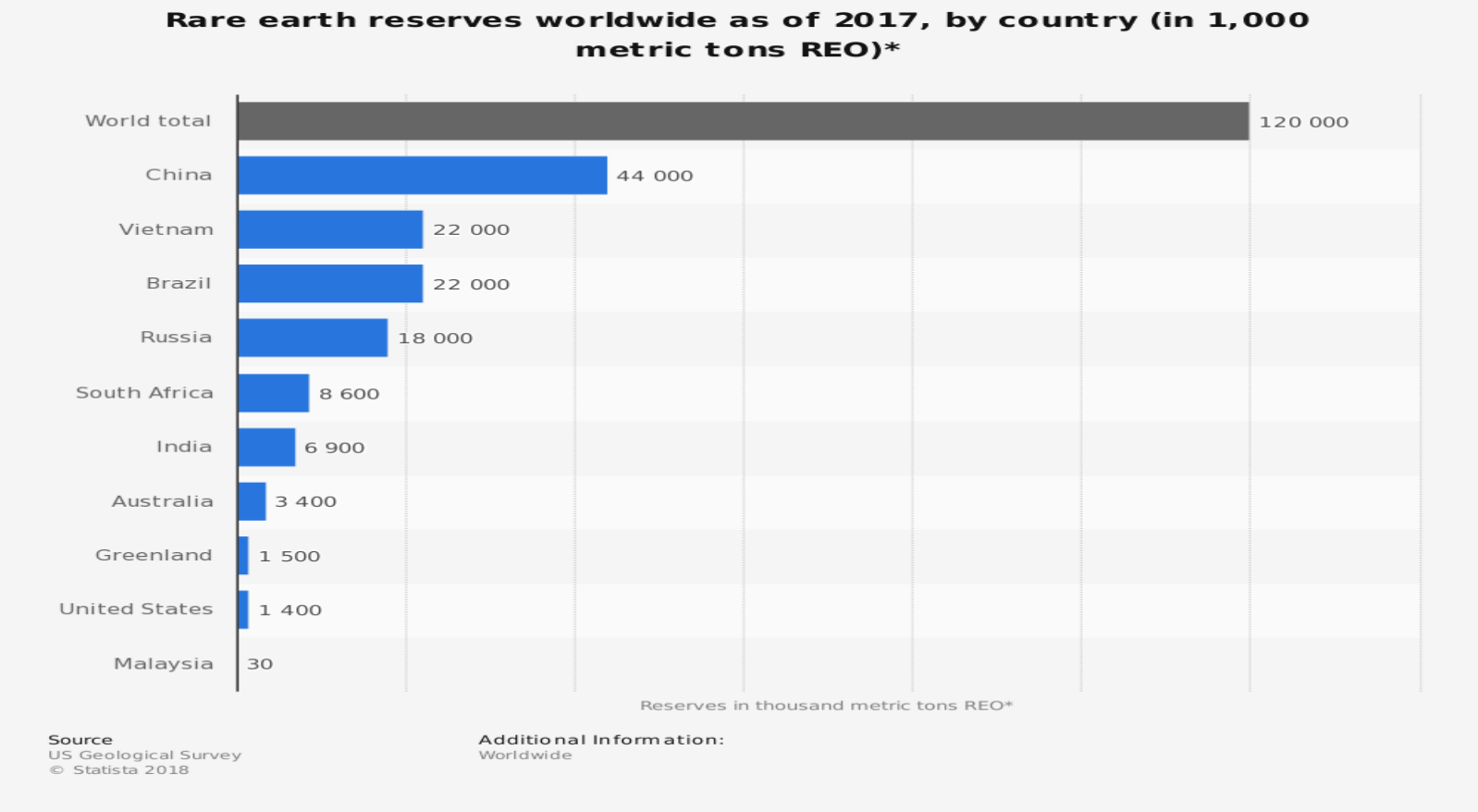
- Introduction to Rare Earth Metals and Uses
- Phosphorus breakdown
- Dosing and Chemistry Comparison to Al, Fe-based coagulants
- Case Study Applications
- Review, Discussion, Questions

Rare Earths

- Rare earth elements are located in the lanthanide series (plus Sc and Y) of the periodic table
- Most prominently known for high magnetic strength
- Unique reactivity with oxyanions, such as phosphate
- Rare Earth Elements are not very rare. Cerium is the 26th most abundant element, making up 66 ppm of the Earth's crust, half as much as chlorine and five times as much as lead.



Worldwide REE Reserves by Country



120mm tons in total reserves will supply market for up 800 years at current demand levels, approximately 140,000 tons per year

Geographic Breakdown of REE Production

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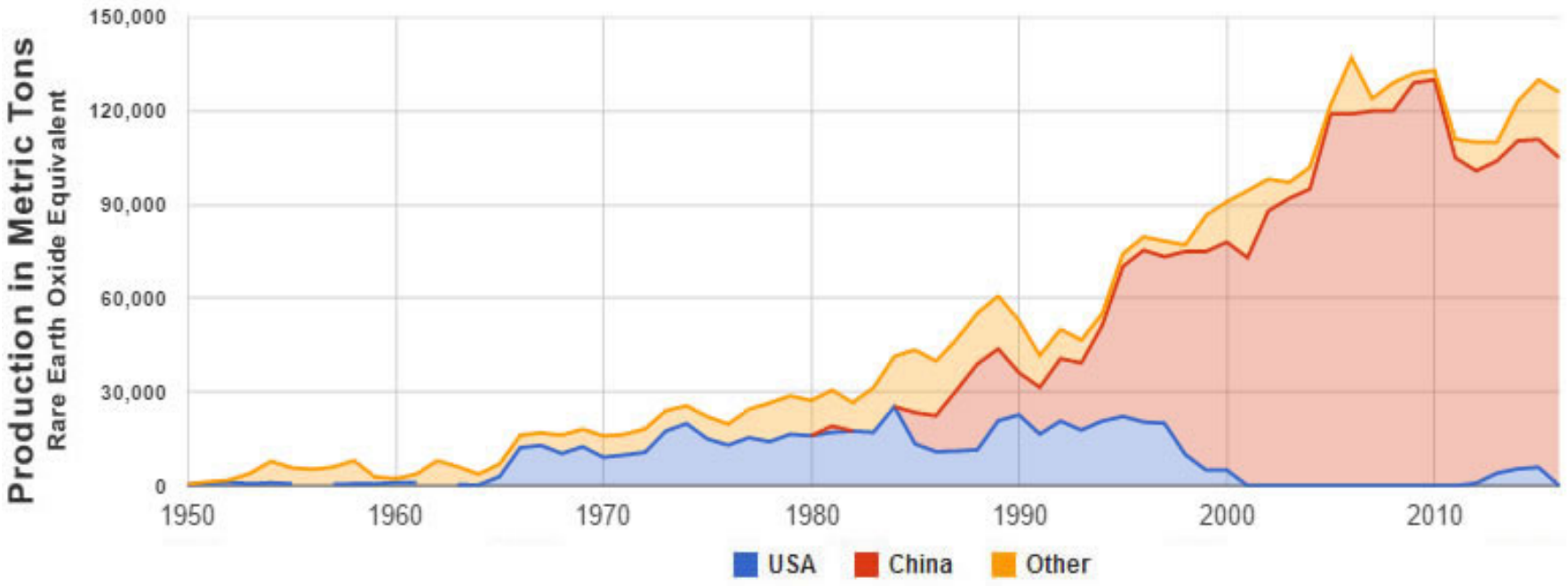
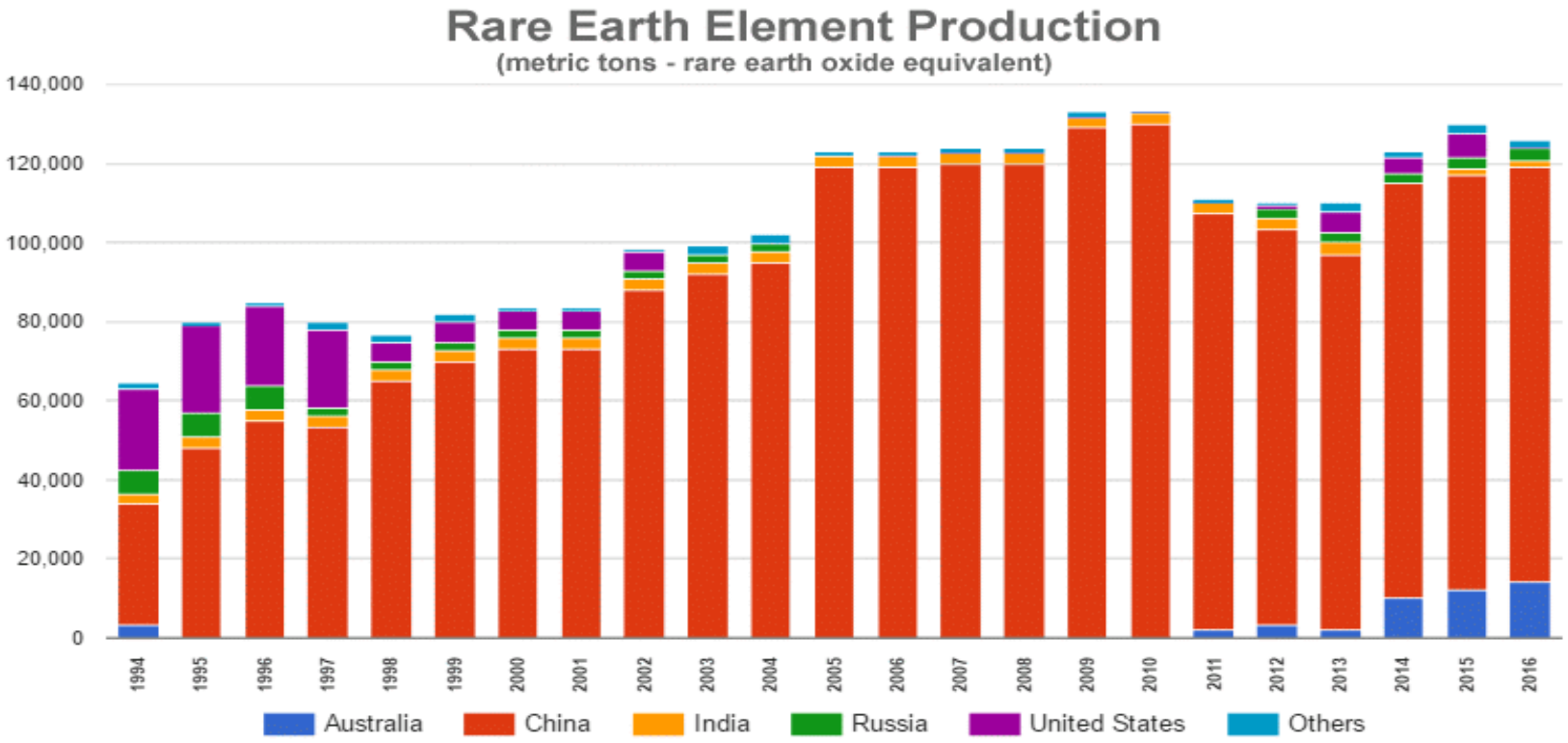


US was a major producer from mid 1960's until 2000.
China began production in 1980 and now dominates the market
Australia, India, Russia and Vietnam are the primary others

More Recent Production by Country



Mt Pass restarted in 2012 and shut down in 2016

Australia becoming a larger player since 2011 and currently planning expansion

Notice the drop in production for 2011, 2012 and 2013, more to come on that

2016 Rare Earth Demand by Application

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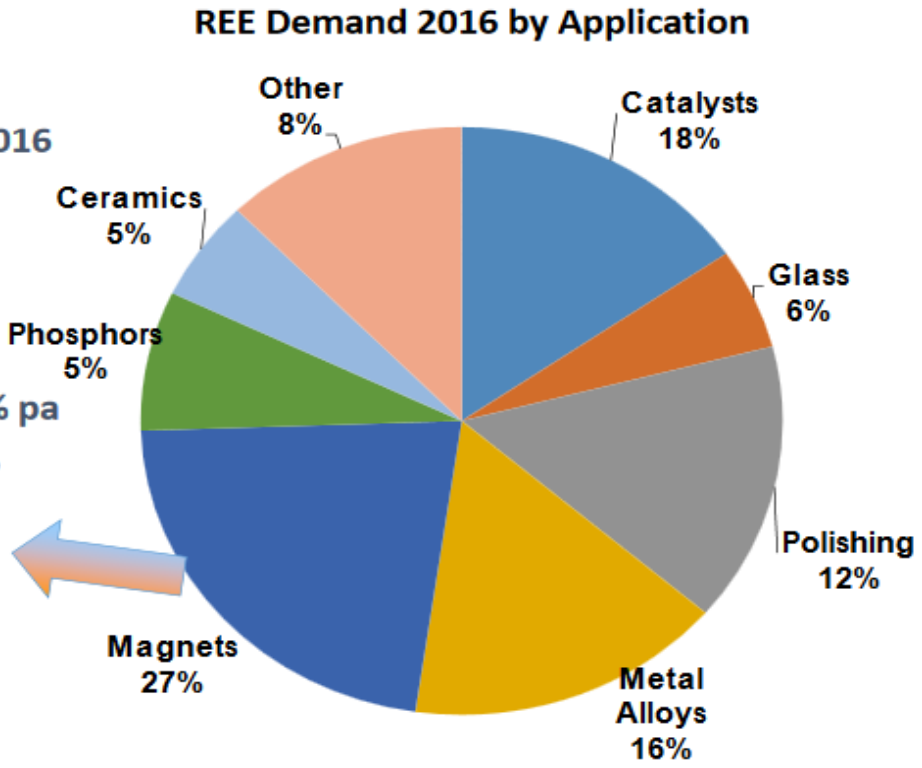
Rare Earth Demand Drivers

- US$3-5B Global market
- 159,500t Annual consumption 2016
- 6-8% Annual growth estimates
- 85-90% REE produced by China

- Permanent magnets dominate consumption and growth 6 - 12% pa
- Annual magnet market ~US$20B
- Major use for Nd, Pr, Dy and Tb
- 80% by value 20% by volume

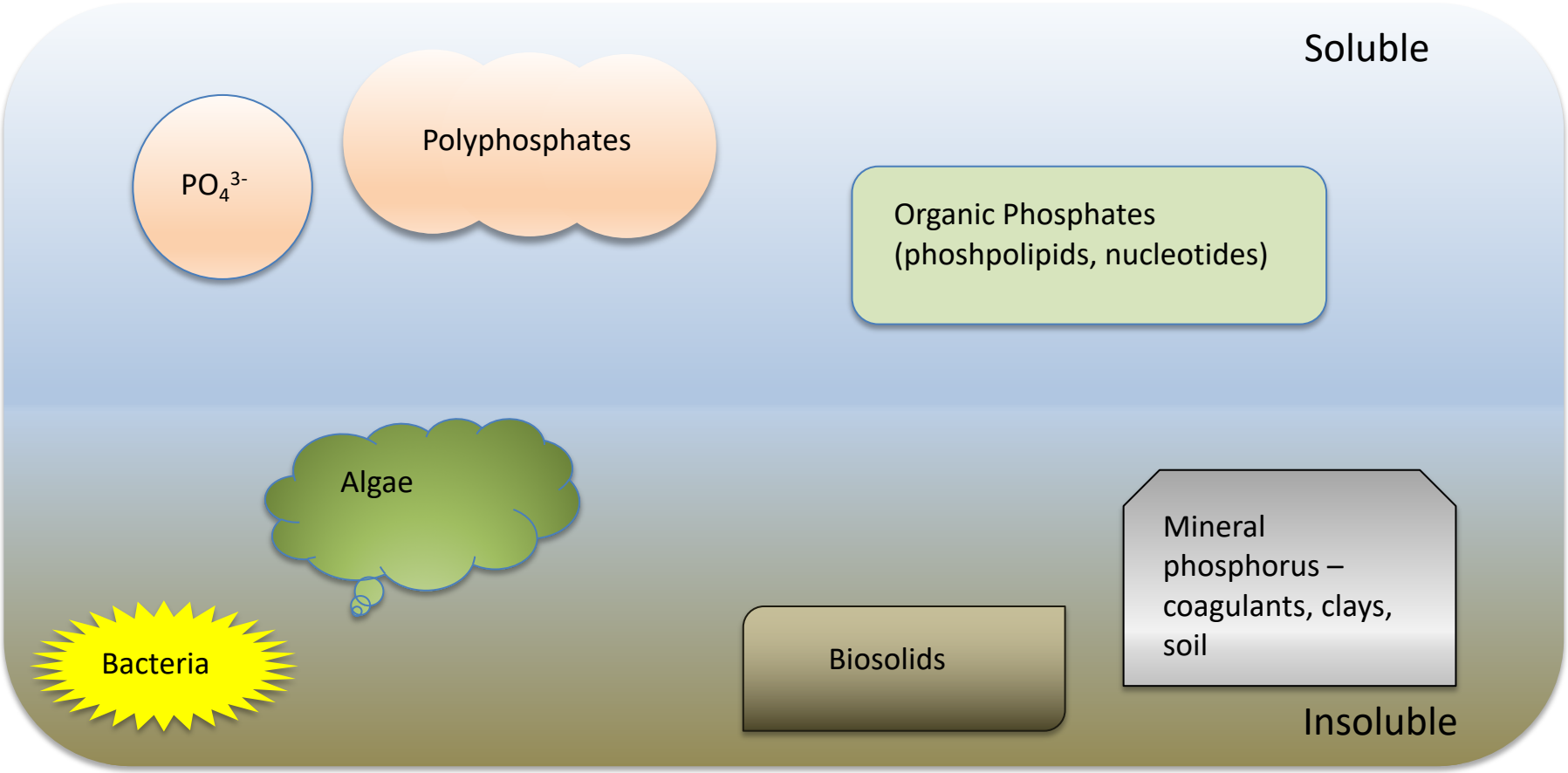
- Growth in other REs for special metal alloys and ceramics



Ce/La used in Catalysts, glass additives, polish and some metal alloys. Nd/Pr used in magnets. Phosphors being replaced by LED, Ceramics mostly as color pigments

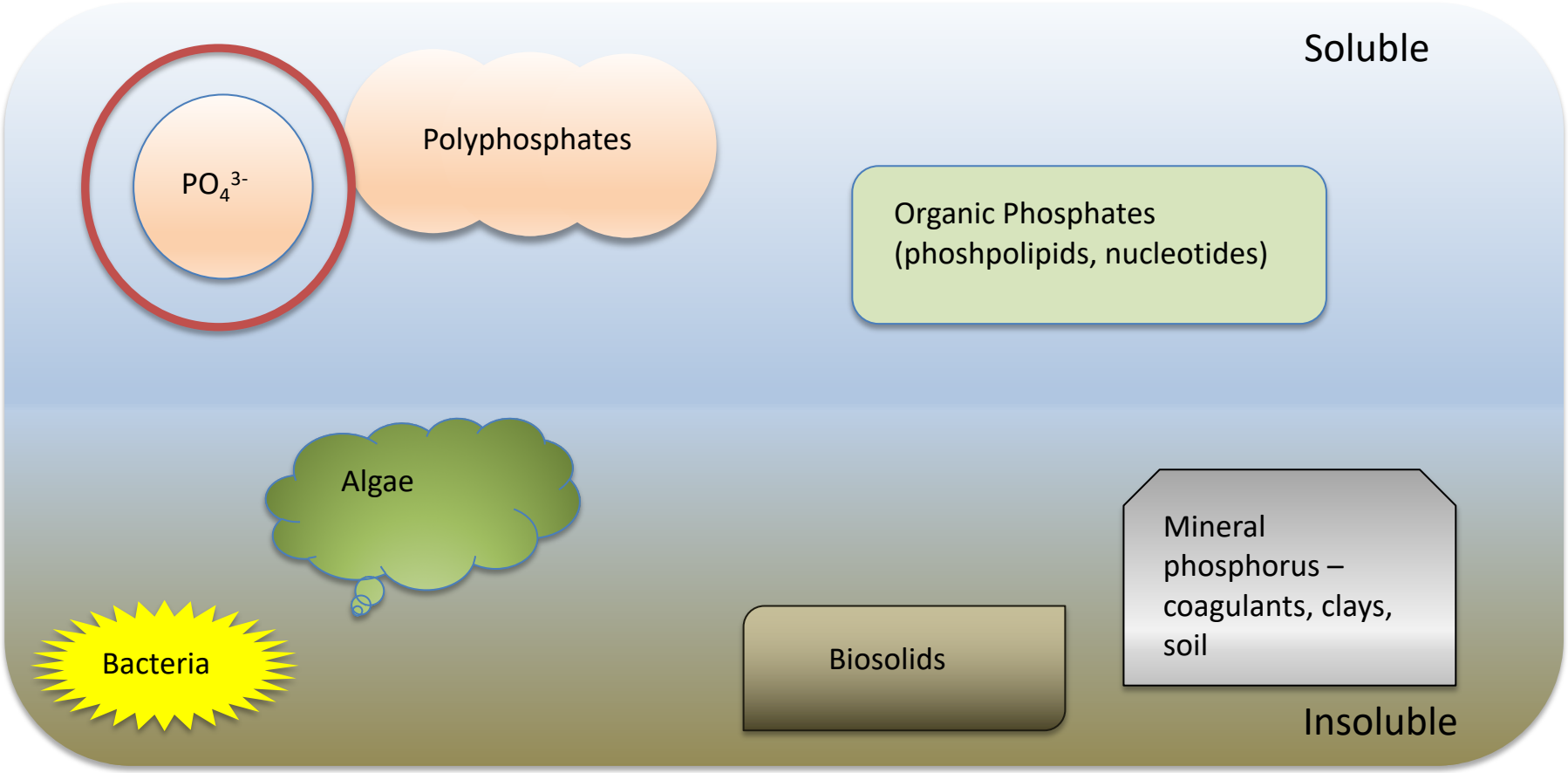
- Phosphorus breakdown

Total Phosphorus (TP) measurement



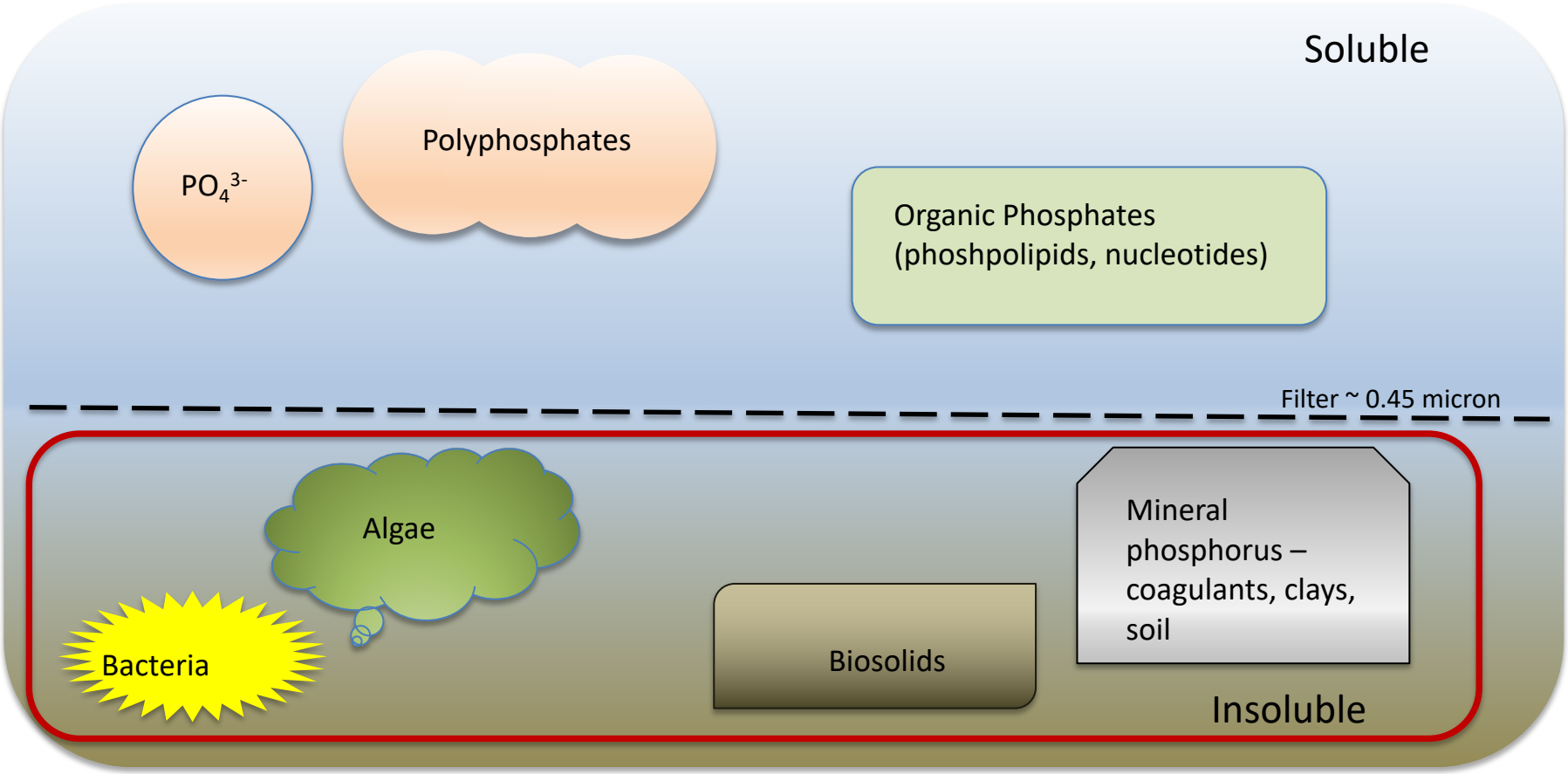
- TP is a measure of all elemental phosphorus in an unfiltered sample
- TP = Includes all soluble + insoluble
- TP = Reactive + unreactive phosphorus

Ortho-Phosphorus OP



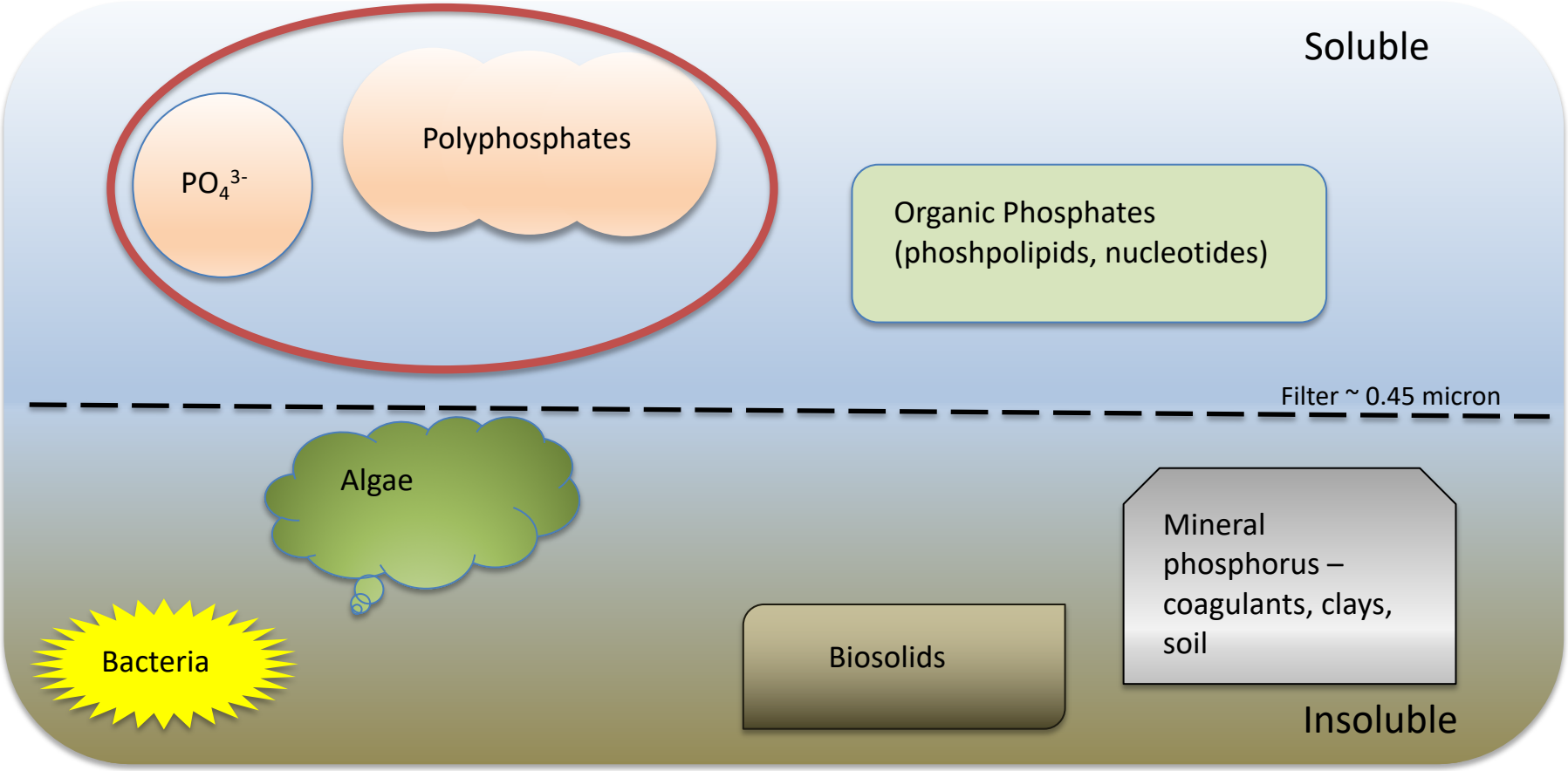
- OP = Soluble
- OP = Reactive
- Removed by chemical coagulation

Insoluble Phosphorus



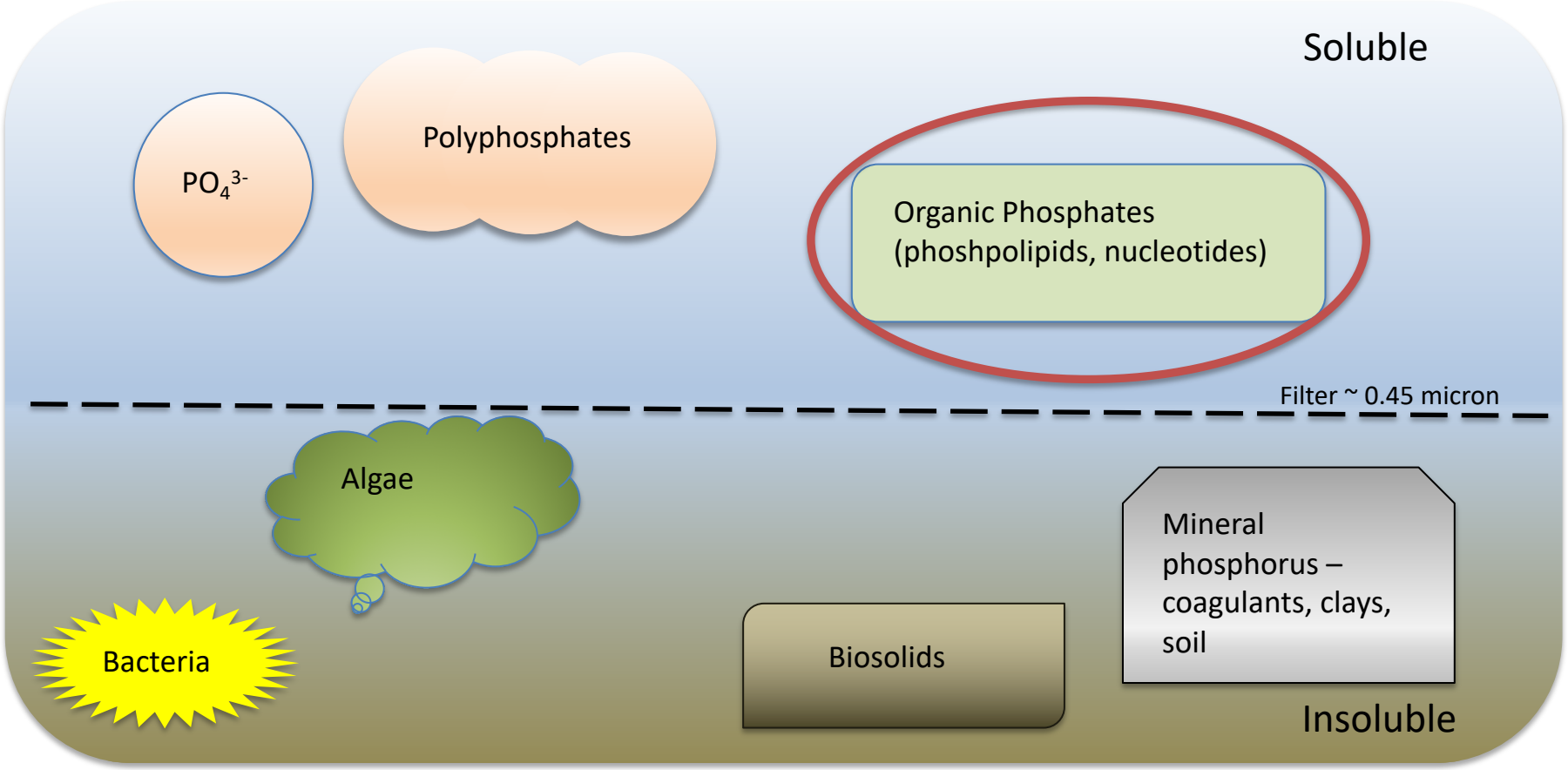
- Insoluble phosphorus is removed by .45 um filtration
- Also called particulate phosphorus
- Insoluble phosphorus = Reactive + unreactive
- Removed in clarifier

Soluble Reactive Phosphorus – SRP



- SRP = soluble + reactive
- SRP =/= insoluble or unreactive phosphorus (organic phosphates)
- Removed by chemical coagulation

Soluble Non-reactive Phosphorus (sNRP)

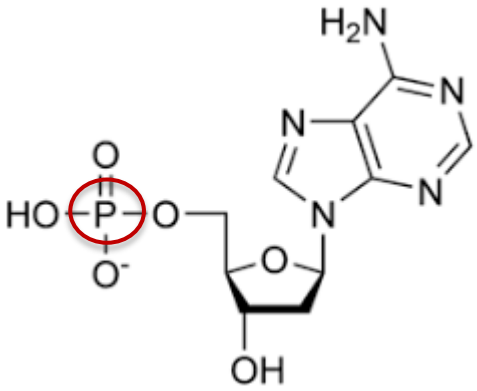


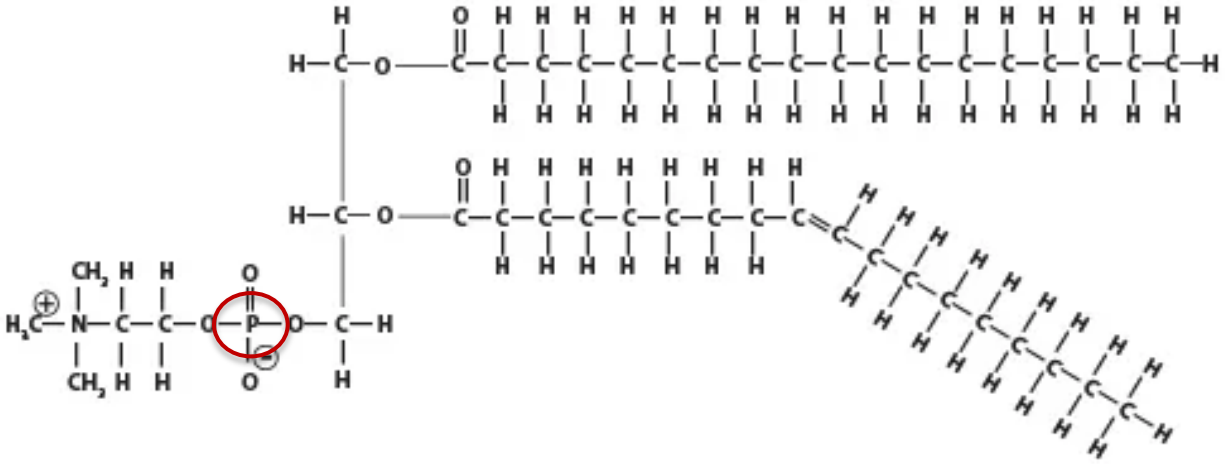
- sNRP = soluble + non-reactive phosphorus
- Calculated from other P measurements (Soluble total P – SRP)

Difficulty of sNRP

Why is SNRP important if it is a small fraction of TP?

- Cannot be removed by filtration
- Cannot be removed by chemical coagulation
- Not available for biofiltration
- A high concentration (>0.3ppm) of sNRP can prevent a facility from ever reaching a permit level





- Dosing and Chemistry Comparison to Al, Fe-based coagulants

Fast Coagulation Properties

- Molecular weight of rare earth vs. traditional chemical coagulants is much higher

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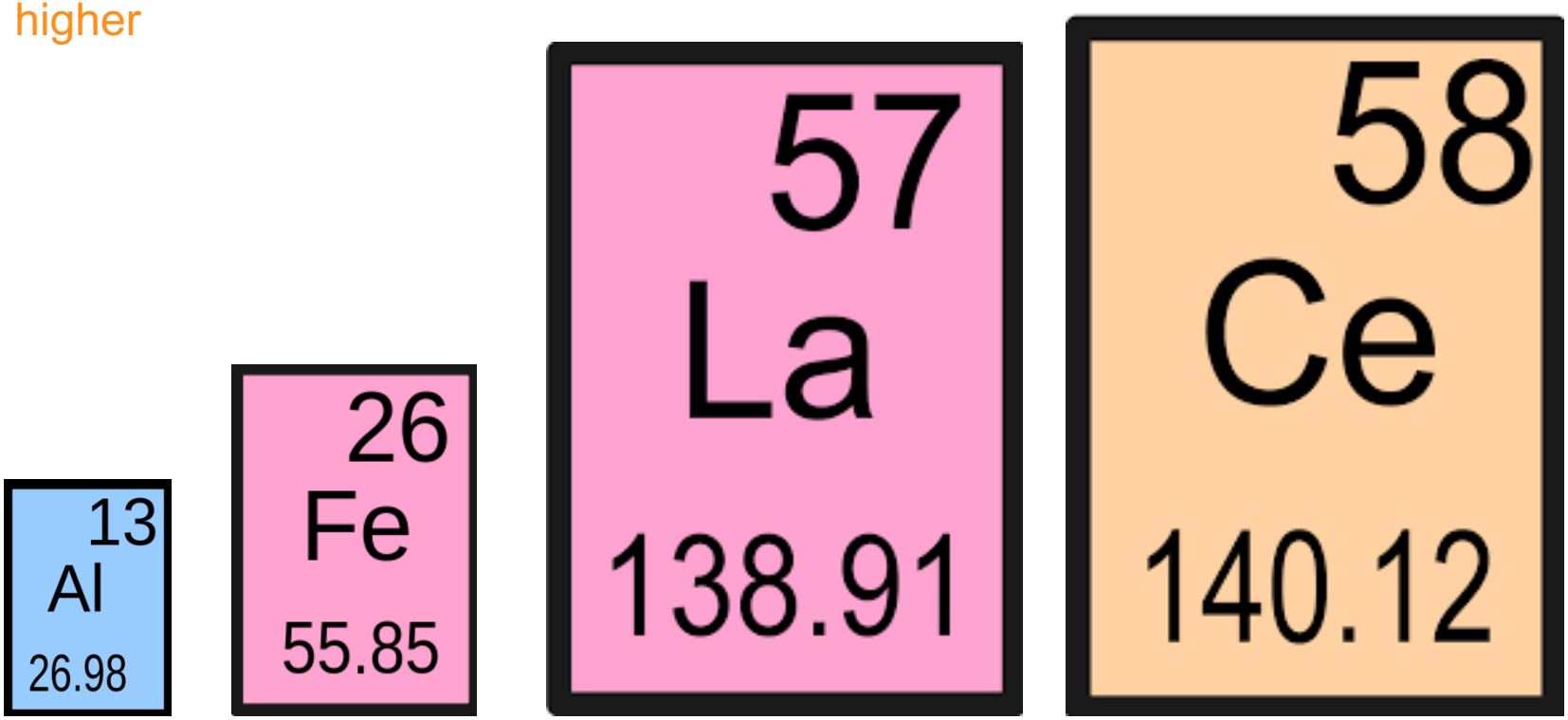
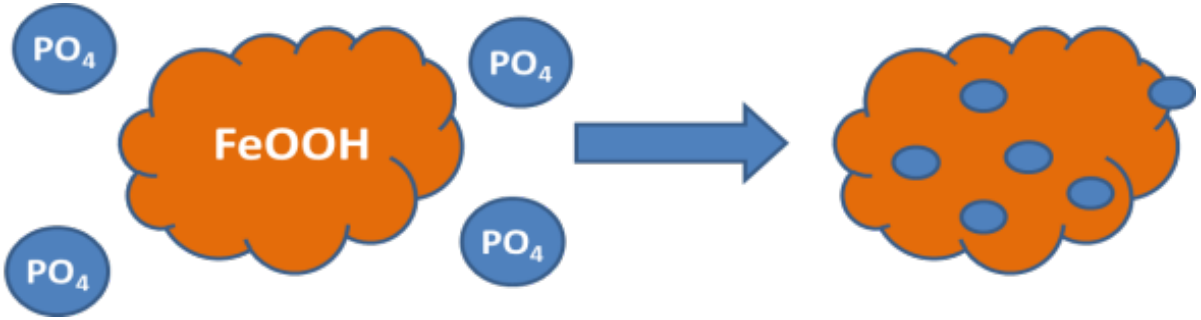


- Forms denser precipitate which settles well in clarifier

Phosphorus Removal Mechanism

- Rare earth elements form strong, crystalline bonds with phosphorus
  - Forms insoluble rhabdophane precipitate

- Iron and aluminum based products form amorphous “cloud” in solution
  - Adsorbs phosphate onto metal hydroxide floc

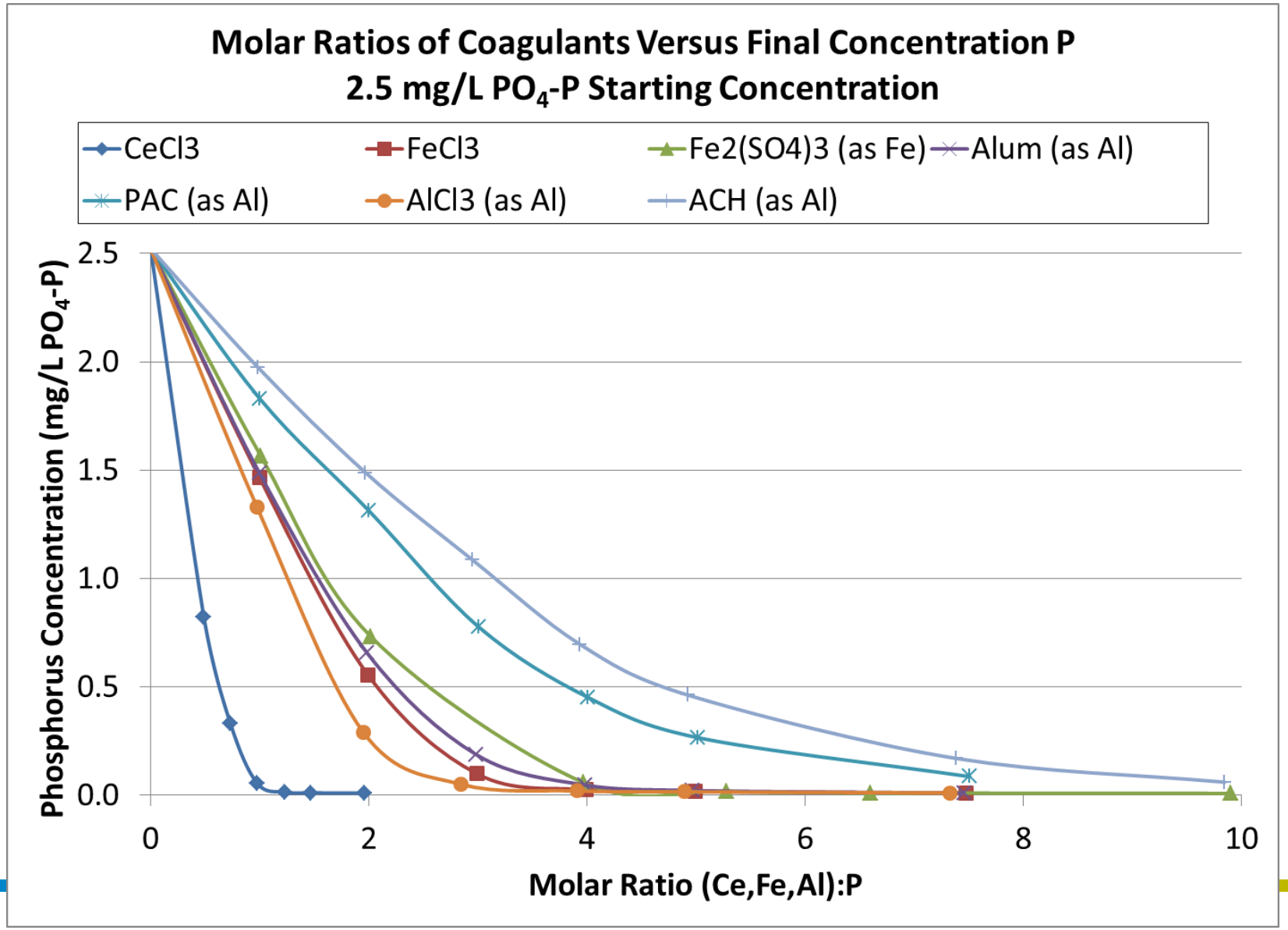


Why RE is different than traditional coagulants

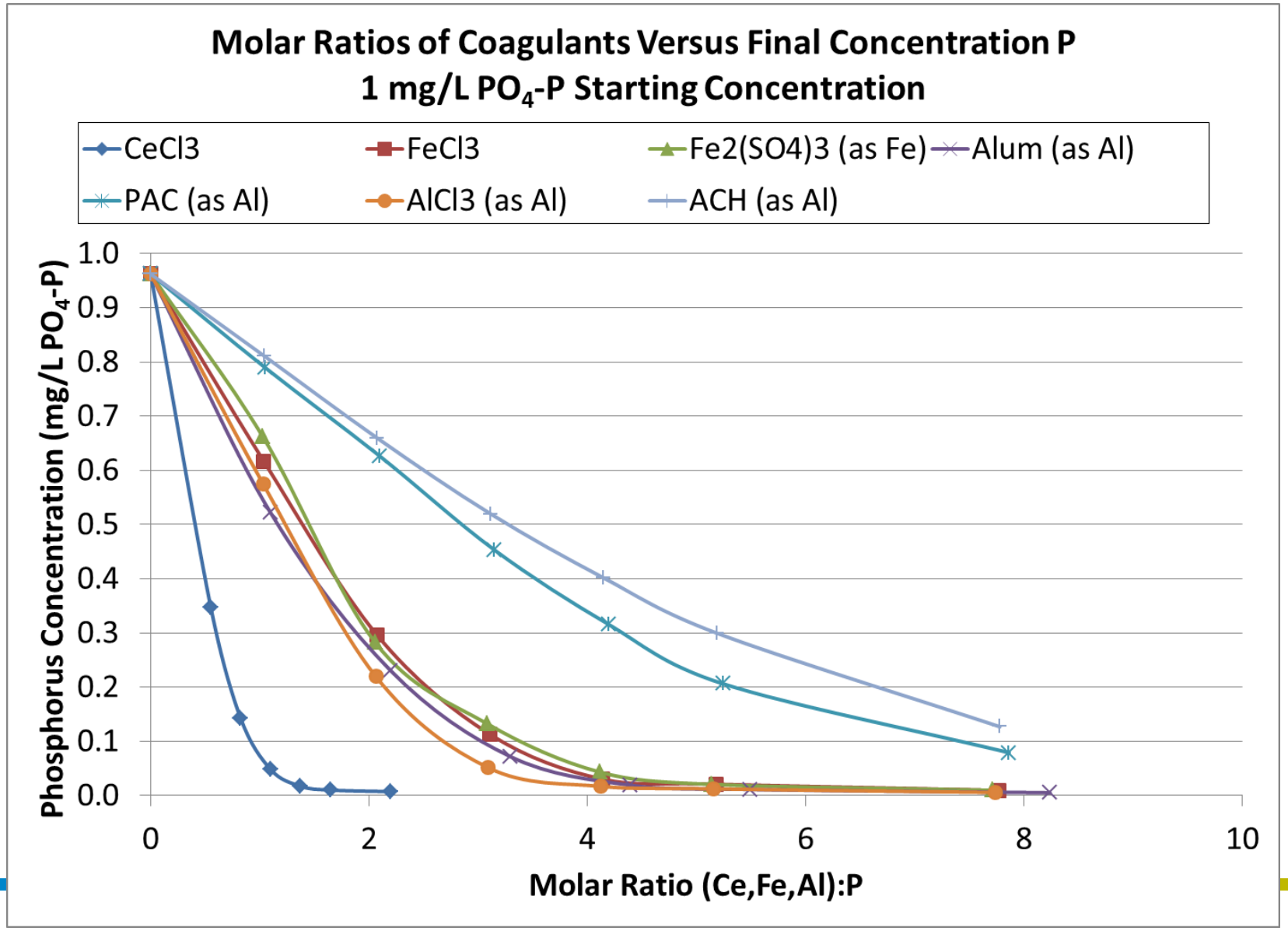
- Precipitate is $CePO_4$ / $LaPO_4$ (Rhabdophane)
- Forms ionic bonds
- Preferentially reacts with phosphorus
- Achieves a 1:1 molar ratio of Rare Earth:PO_4 → Reduced chemical sludge

- Forms Fe/AlOOH and Fe/$Al(OH)_3$ intermediates to adsorb P
- Phosphate adsorbs on the surface of the floc (surface chemistry)

Coagulant Comparison – 2.5 mg/L



Coagulant Comparison – 1 mg/L



Solids Handling

- Less coagulant volume required to reach phosphorus limits.
  - 30 to 70% reduction based on traditional coagulants
- Improved dewatering of biosolids – less water molecules
  - Increase Belt Filter Press 15-17% to 23-25%
  - Centrifuge: 21-23% to 25-29%
- Creates a Denser Sludge
  - Increase percent solids in sludge holding tank

pH

- pH scale is a measure of acid and base concentration. It ranges from 1 to 14 with 7 considered neutral.
- The pH scale is logarithmic which means that every integer change results in a 10x higher acid or base concentration.
- Rare earth chloride is stable in a solution of 3 to 4 pH.
- Other coagulants often have a pH of 1.5 to 2.2.
- Rare earth chloride is 100 times less acidic than other coagulants due to the logarithmic nature of the pH scale.

Alkalinity

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- Alkalinity is the ability of a solution to resist pH changes when an acid is added.
- Rare earth chloride is 100 times less acidic than other coagulants.
- Rare earth chloride replaces other coagulants with a dose volume 25% or less.
- These two mechanisms combine to result in a reduction of acid addition of 300-500 times.
- Rare earth chloride reduces chemical alkalinity consumption by several hundred times leaving more alkalinity for denitrification.

Toxicity concentrations

Ecotoxicity:

Toxicity to fish	Fathead Minnow 96–hour LC50: 191 mg/L NOEC(96 hr): 125 mg/L 7-day IC25: 2.1 mg/L NOEC(7 day): 1.3 mg/L LOEC(7 day): 2.5 mg/L
	Rainbow Trout
96–hour LC50: 10.4 mg/L	NOEC(96 hr): 5.0 mg/L
Toxicity to daphnia	Ceriodaphnia dubia 48–hour LC50: 16.4 mg/L NOEC(48 hr): 7.8 mg/L 7-day IC25: 2.0 mg/L NOEC(7 day): 1.6 mg/L LOEC(7 day): 3.1 mg/L

- Typically dosed in the WWTP system at a ratio of 1 gallon RE300 per 53,000 gallons of wastewater
- This yields a system concentration of 12mg/L RE
- Whole Effluent testing has shown steady state RE concentrations of 0.049 g/mL and 0.11 g/mL .
- Over 99.2% of the RE that gets injected into the WWTP leaves the system in the sludge and not the effluent.

Toxicity continued – medical uses - Lanthanum Carbonate

- Pure lanthanum carbonate is commonly used as an ingested medication for kidney disease. In the acidic environment of human digestion, lanthanum carbonate dissociates and makes the lanthanum available to bond with phosphate. This process removes phosphates from the blood and the digestive tract to ease the filtration load on the kidneys. The process forms lanthanum phosphate which has proven to have very low toxicity.

- Given the similar chemistry of lanthanum and cerium, there is no reason to believe cerium would have different toxicity properties.

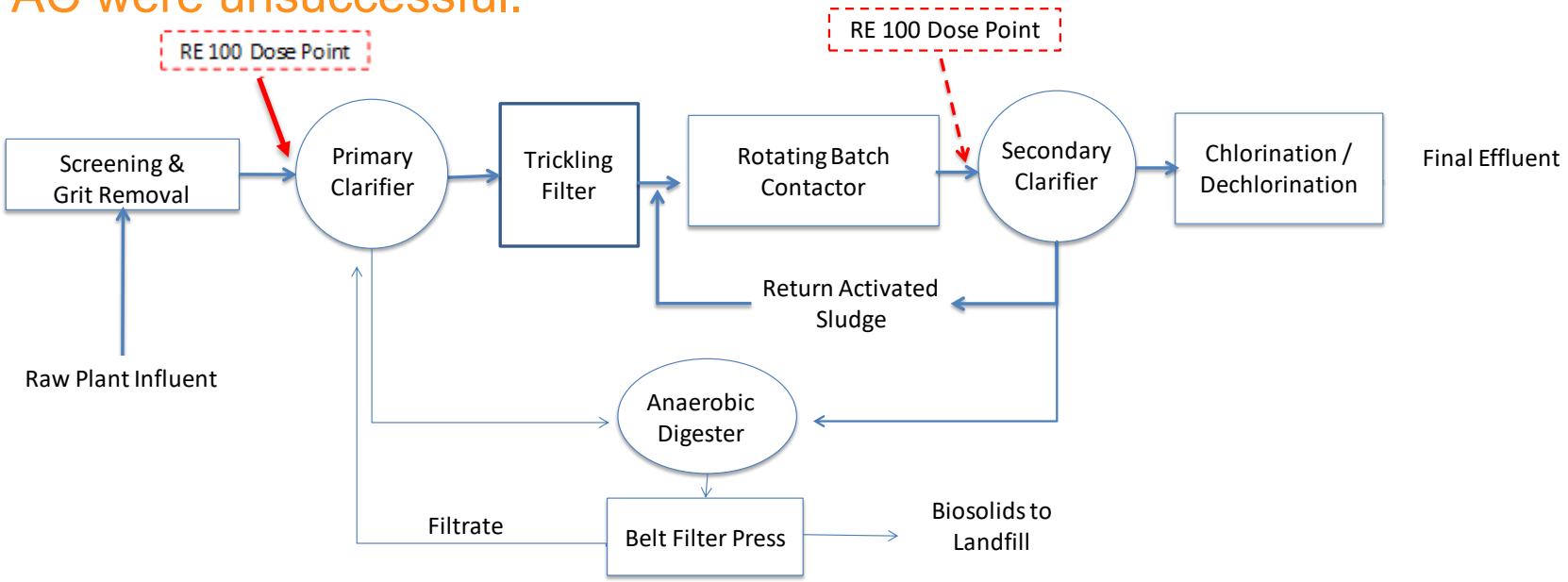
Corn Study

- This is a research document that compares corn grown in a native soil, corn fertilized by Fe treated biosolids, and corn fertilized by RE treated biosolids
- The Results show that P availability in the soil is comparable to Fe as well as no more RE uptake in the plant biomass than the control sample grown in native soil (RE naturally occurring).
- The Results also show now difference in corn yield between samples
- This test concludes that RE treated biosolids are as safe for land farm applications as Fe treated biosolids.

- Case Study Applications

Borough of Albion, PA WWTF

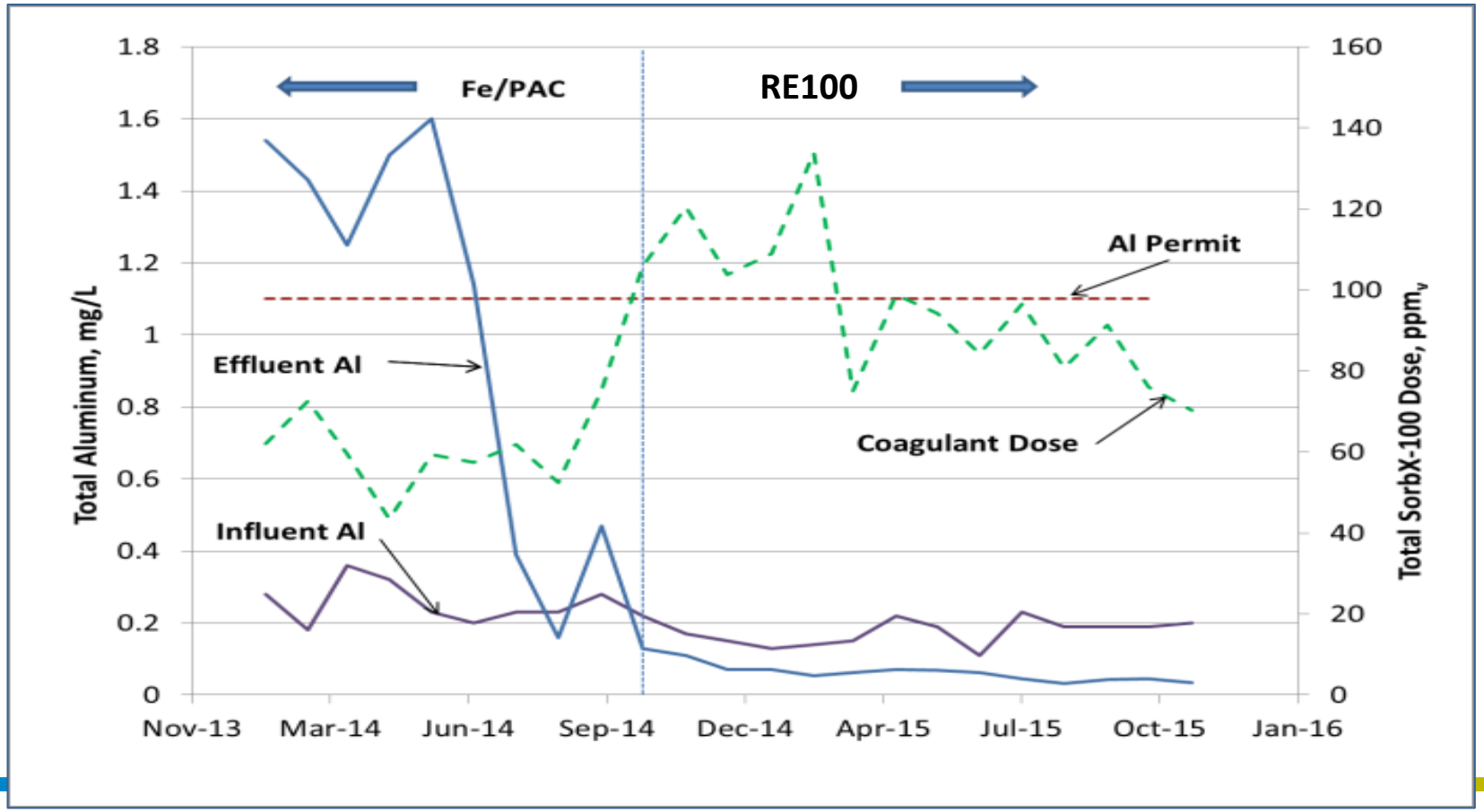
- 0.8 MGD municipal WWTF located in Pennsylvania
- Difficulty meeting phosphorus & aluminum permit levels
  - Total P limit of 1.0 mg/L mg/L-P
  - Total Al limit of 1.1 mg/L
- Attempts to meet the permit by increasing the dosage rate of ferric or PAC were unsuccessful.



Borough of Albion, PA WWTF

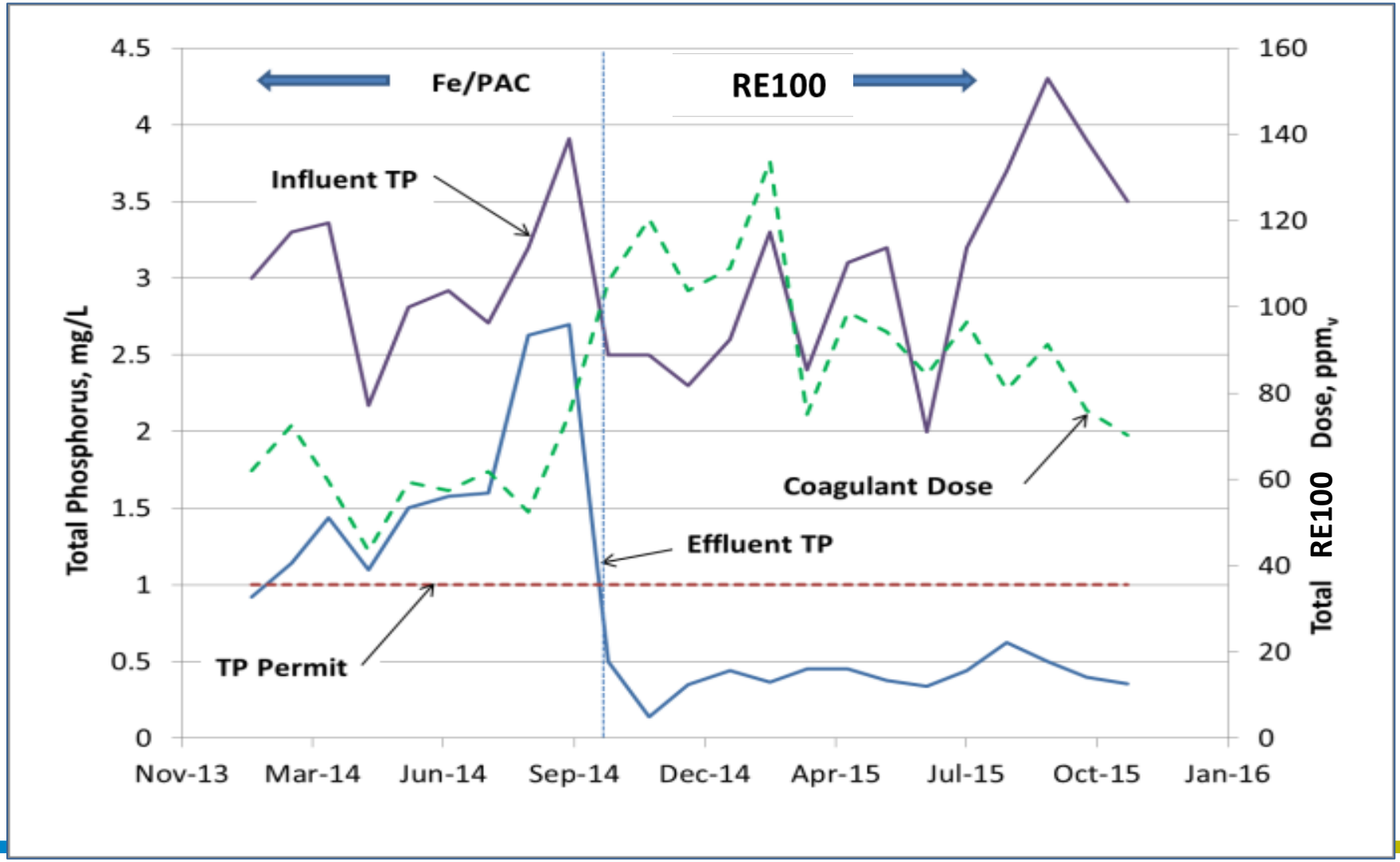
- RE100 has allowed Albion to achieve compliance for phosphorus and aluminum discharge permits since Sept 2014

- Aluminum levels before & after RE100

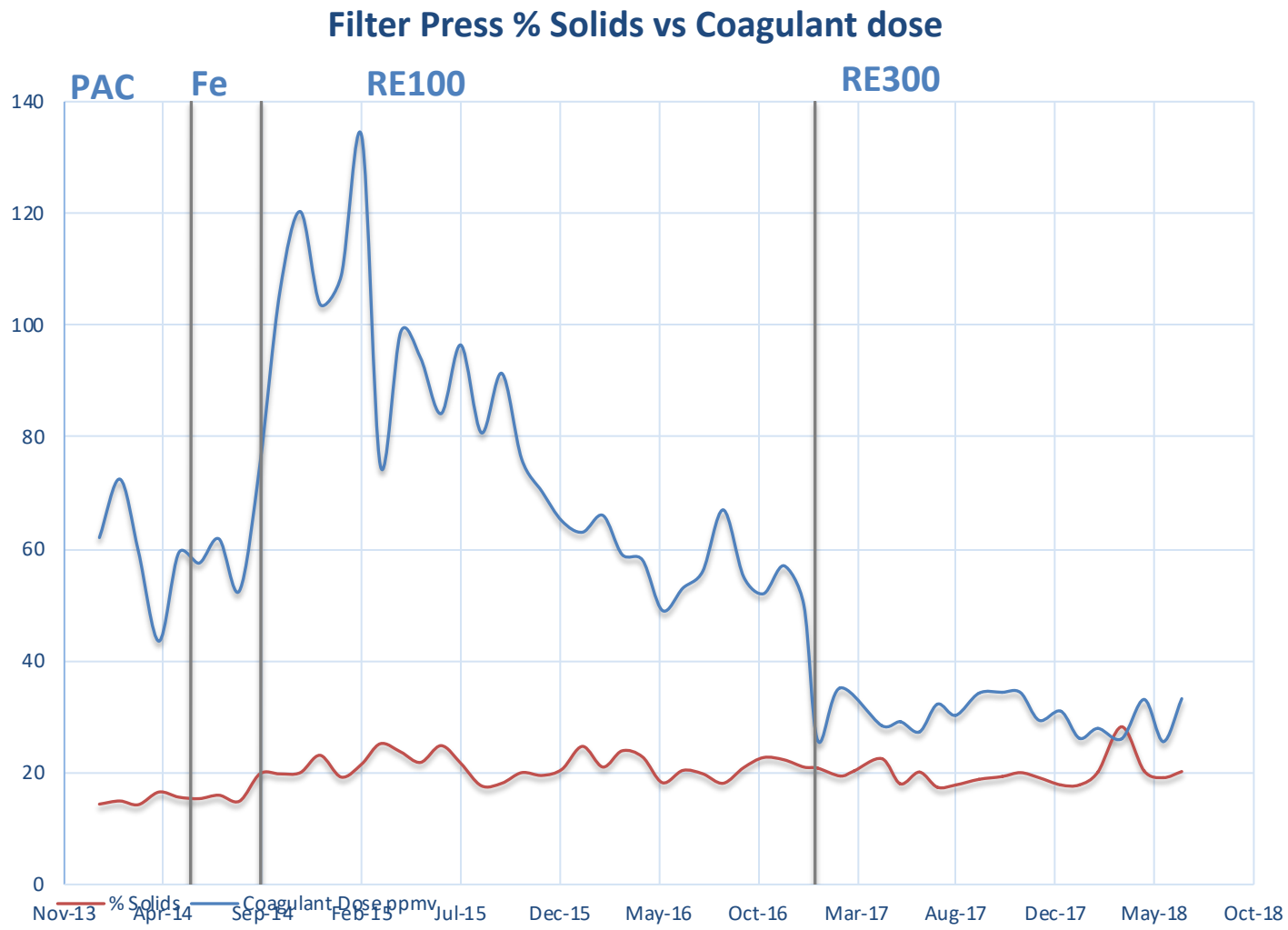


Borough of Albion, PA WWTF

- Total Phosphorus levels before & after RE100



Borough of Albion, PA WWTF



RE300 Benefits - Borough of Albion, PA WWTF

- RE100 has allowed Albion to meet its meet phosphorus and aluminum discharge permits & remain in compliance since Sept 2014
- Improved coagulation & settling in clarifiers
- Significant decrease in sludge volume
  - 68% savings on the sludge disposal costs/ year
    = $70,000/year annual savings
- Improved performance on belt filter press
  - Prior to RE100, ran belt filter press 5 days/week
  - With RE100, run only 1 day/week
  - Energy savings (estimated to be $7K/year)
- Dose approximately 3 GPD in Primary and 20 GPD in Secondary

Struvite

- Struvite is a mineral that forms at a 1:1:1 combination of phosphate, magnesium, and ammonia, and growth is accelerated at pH of 8 or higher
- Plant is targeting 100 mg/L as phosphate limit for struvite formation. During winter months they use RE to reduce phosphate below this level.
- Without sufficient phosphate in solution, struvite does not have the ingredients needed to grow.

Struvite Control – Centreville VA

Struvite build up on pump impeller after just 15 days

Struvite growth in pipe. ID decreased from ~4” to 2”

Struvite manually removed from centrifuge

1 year results – RE to prevent struvite

After 1 year of struvite prevention with RE, the pump and pipe show no signs of struvite growth compared to just 18 days of use shown previously. The centrifuge did show struvite growth, but it was characterized as minor, soft, and was washed off with a hose.

Village of Geneseo NY

- In, 2017, Village of Geneseo was a .8 – 1.0 MGD facility without a current phosphorus limit
- Began pursuit of a capital project to meet a pending 1.0 mg/l TP limit.
- Capital project to add equipment would turn into a multi-million dollar project.

Village of Geneseo NY WWTP

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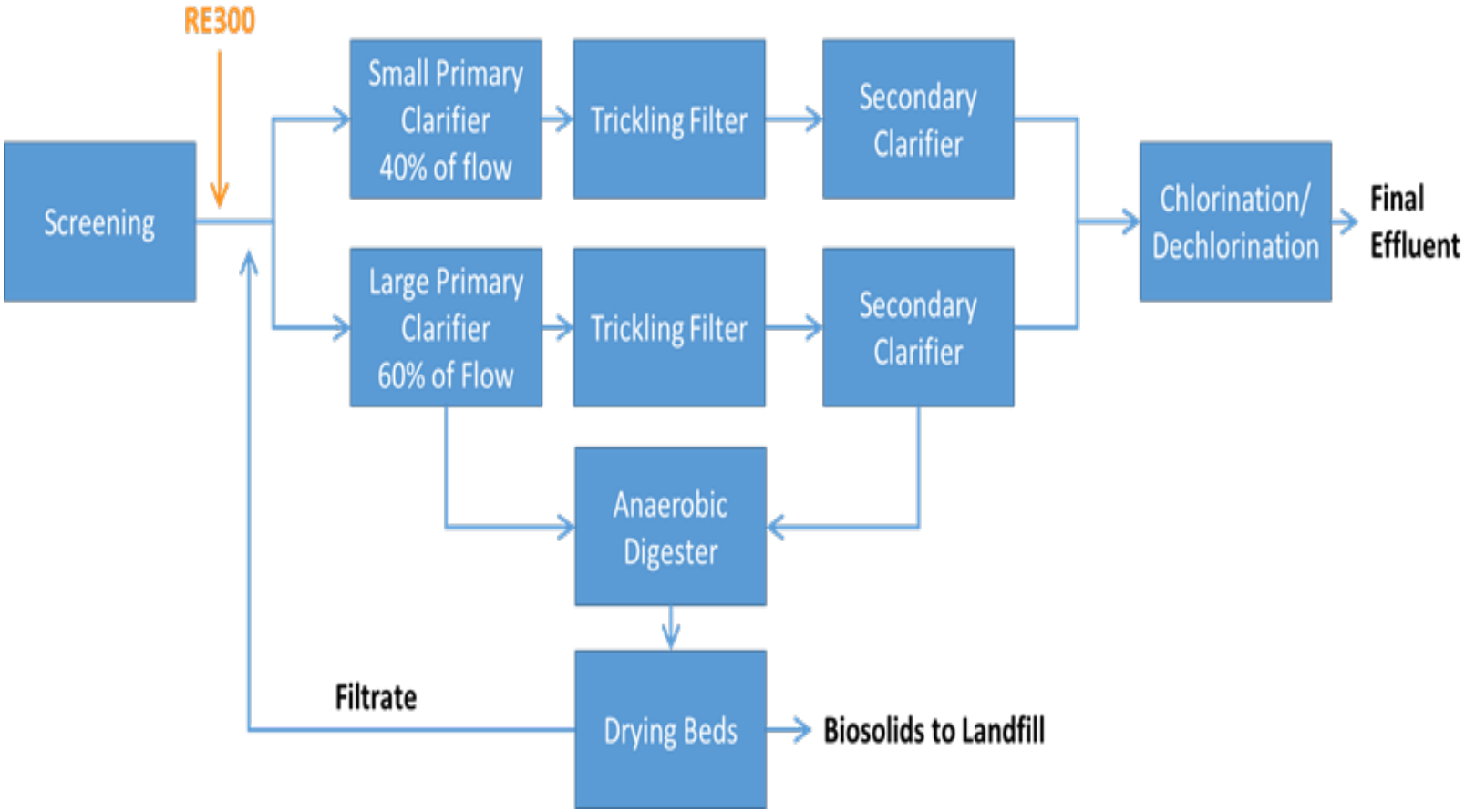

Village of Geneseo NY WWTP

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- Able to dose before primary clarifiers at headworks to have only one dosing point
- Meeting 1.0 mg/l TP limit using 20 or so gallons per day during TP season (May-October)

Key Benefits of Rare Earth Technology

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- ✓ Less coagulant volume required to reach low phosphorus limits
- ✓ Significant reduction in chemical sludge volumes through targeted chemical reaction
- ✓ Improved coagulation – noticeable improvement in water clarity
- ✓ Improved dewatering of biosolids
- ✓ Non-hazardous – safer to work with than iron based products
- ✓ Low corrosivity – less maintenance costs
- ✓ No need for pH adjustment – Low pH of iron and aluminum based products can require addition of pH control chemicals
- ✓ Will not stain or discolor facility structures or equipment
- ✓ Compatible with existing equipment

Questions?

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