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# Wisconsin Case Studies: Using Rare Earth Chloride to Reduce Phosphorus to Ultra-Low Limits

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# Discussion Outline

- **Rare Earth Technology Introduction**
  - What are rare earths?
  - Rare earths vs. traditional P removal
- **Preliminary Lab Studies**
- **Plant Trials**
  - Equipment Set-up
  - Facility processes
  - Trial results
- **Conclusions / Summary**

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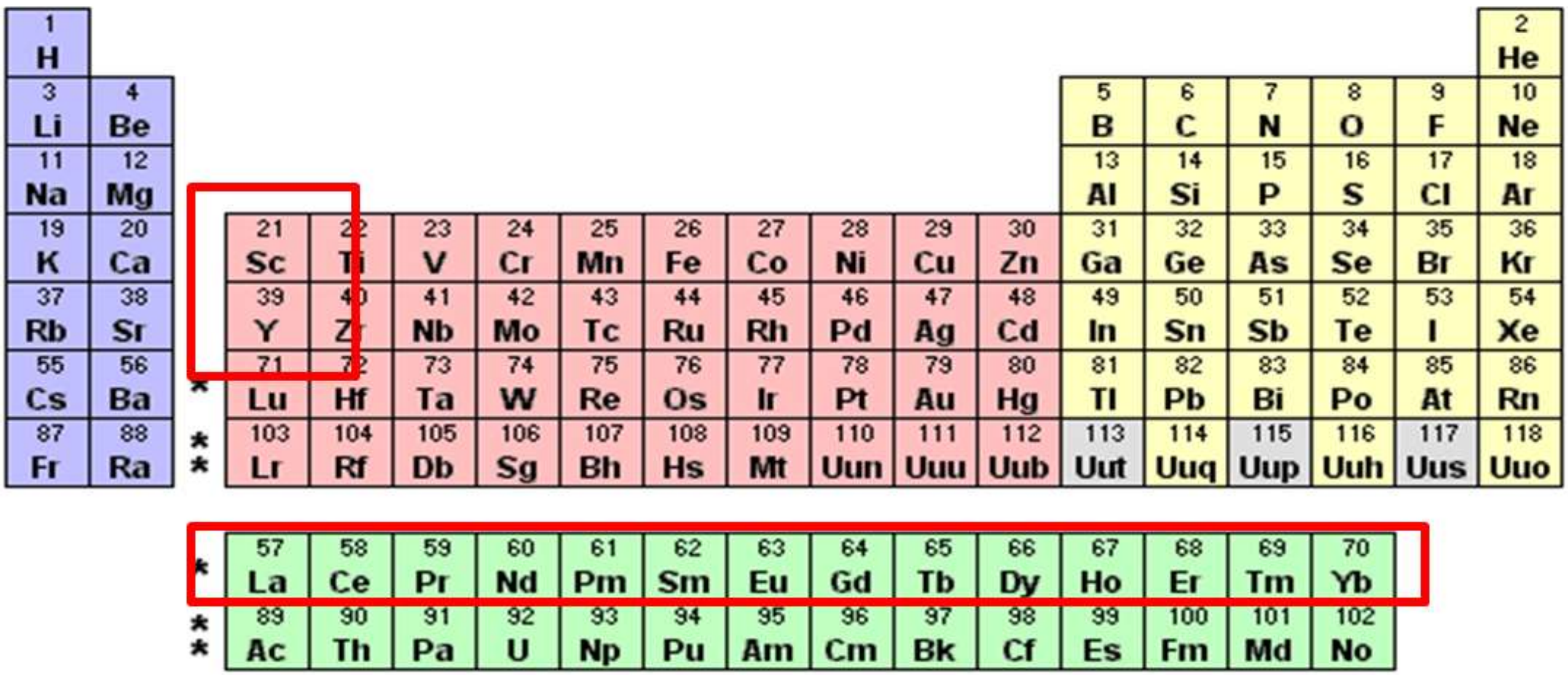
- Rare earth elements are located in the lanthanide series (plus Sc and Y) of the periodic table
- Most prominently known for high strength, permanent magnets
- Unique reactivity with oxyanions, such as phosphate




# Typical Rare Earth Markets

## Chemicals & Oxides

- ✓ Automotive (catalysts)
- ✓ Ceramics
- ✓ Chemical catalysts
- ✓ Consumer electronics
- ✓ Glass polishing
- ✓ Internal sales of magnetic materials
- ✓ NiMH Batteries
- ✓ Petroleum refining
- ✓ Phosphors / Displays / Energy Efficient Lighting
- ✓ Pigments
- ✓ Wastewater Treatment

## Magnetic Materials

- ✓ Automotive
- ✓ Computing / Networking
- ✓ Consumer electronics
- ✓ Home Appliances
- ✓ HVAC systems
- ✓ Industrial Automation
- ✓ Office Automation
- ✓ Renewable Energy Systems
- ✓ Telecommunications

## Rare Metals

- ✓ Aerospace
- ✓ Catalysts
- ✓ Electronics
- ✓ LED Lighting
- ✓ Lithium Batteries
- ✓ Phosphors / Displays
- ✓ Solar Power Cells
- ✓ Super Alloys
- ✓ Superconductivity platforms
- ✓ Wireless Communications

# Uses for Lanthanum & Cerium


## Traditional Markets

Glass Polishing

Hybrid Vehicle Batteries

Catalytic Converters

Advanced Optics

## Emerging Markets

Recreation Water

Wastewater

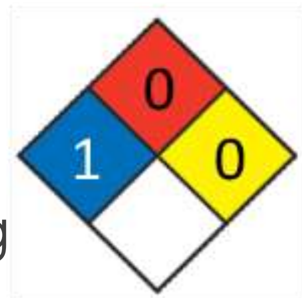
# Why RE is different than traditional coagulants



- Precipitate is $CePO_4$ (Rhabdophane)
- Forms ionic bonds
- Preferentially reacts with phosphorus
- Achieves a 1:1 molar ratio of $Ce:PO_4$

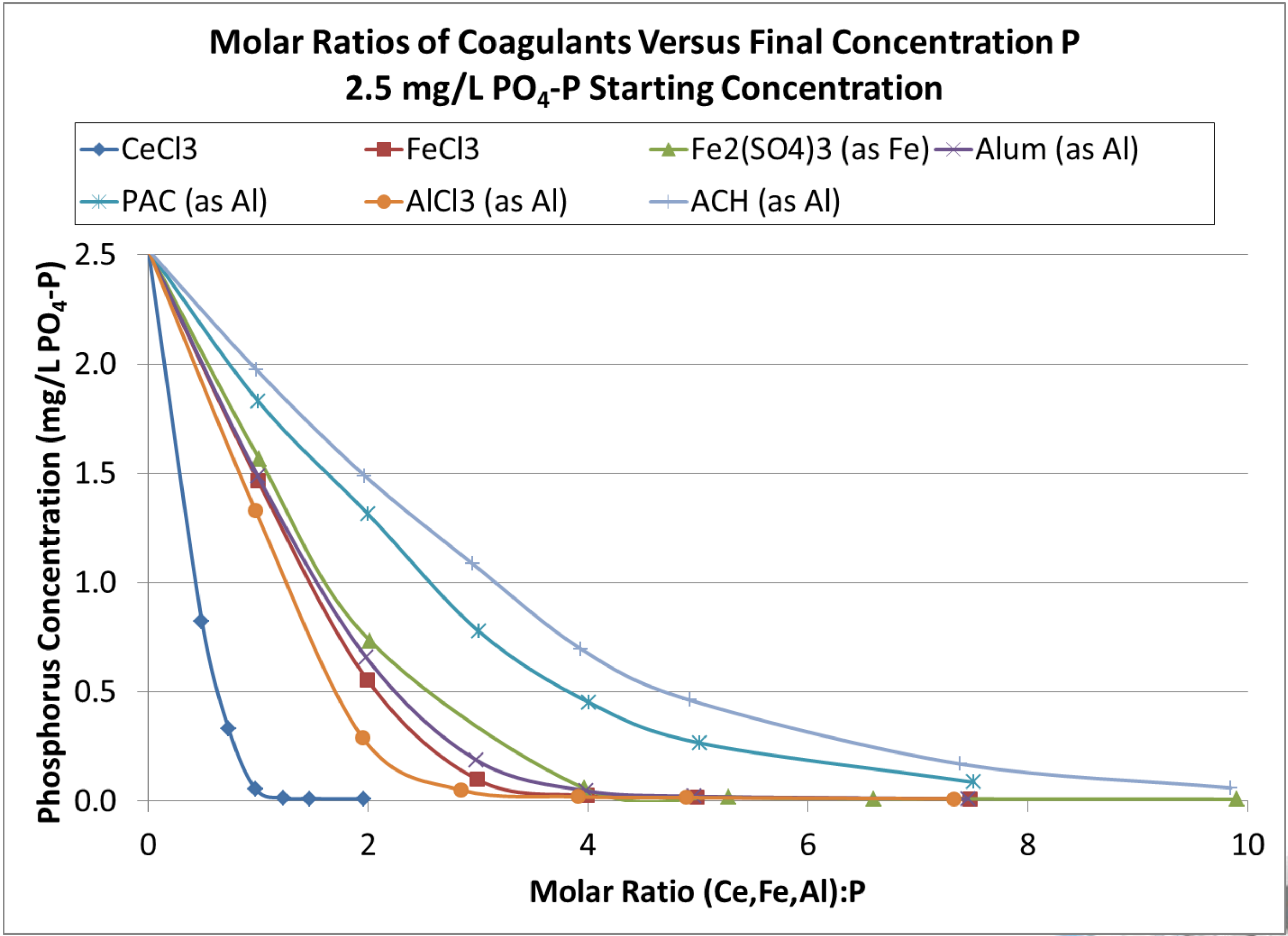
- Forms Fe/AlOOH and $Fe/Al(OH)_3$ intermediates to adsorb P
- Phosphate adsorbs on the surface of the floc (surface chemistry)

- Rare earth chloride solution
- Active Ingredient: Cerium Chloride ($CeCl_3$ )
  - Concentration: 31.5%
- Density: 12.4 lbs/gal
- Freezing Point -40°C
- pH: 3.5
  - Non-hazardous rating

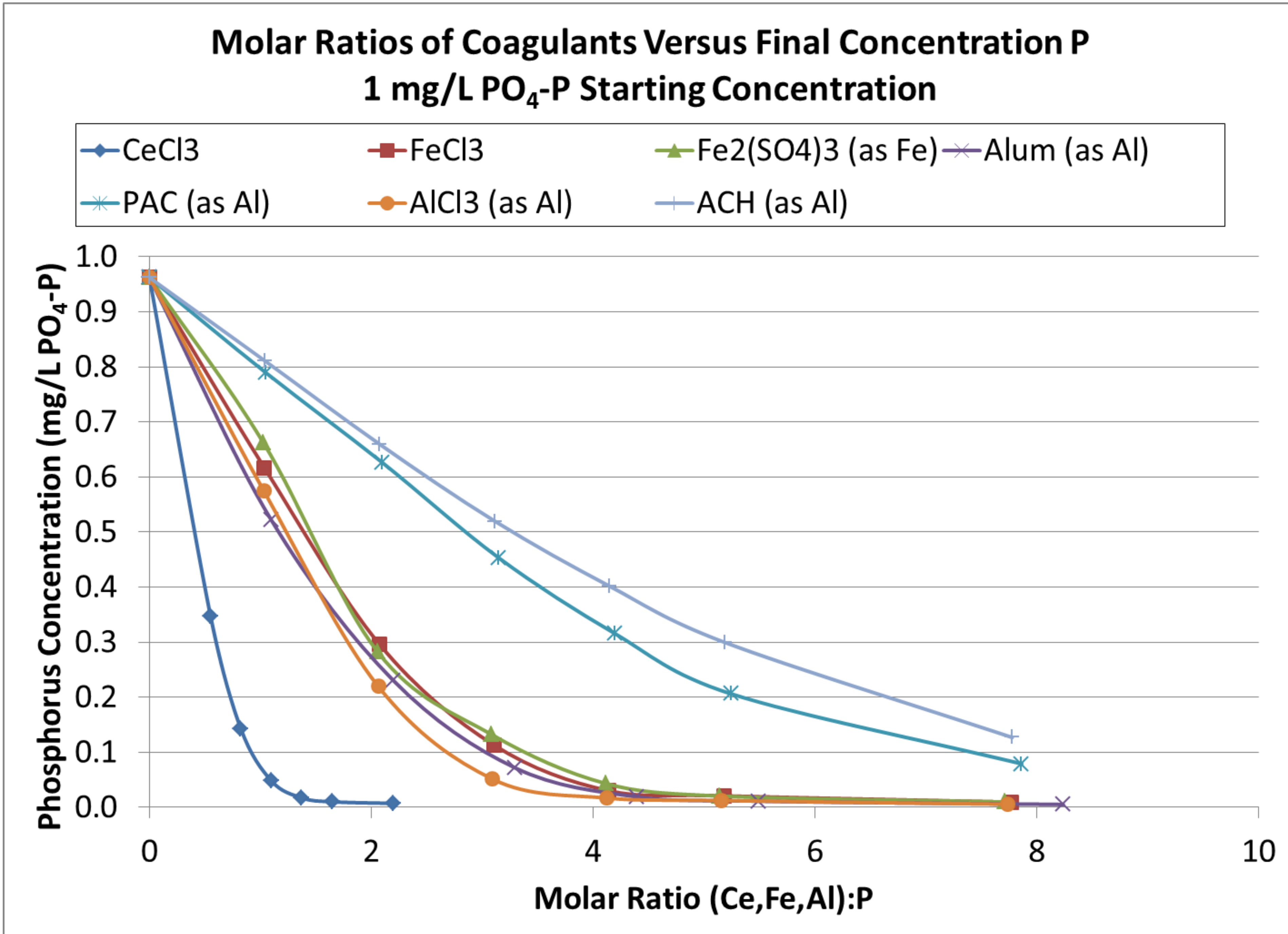



- Compatible with existing equipment

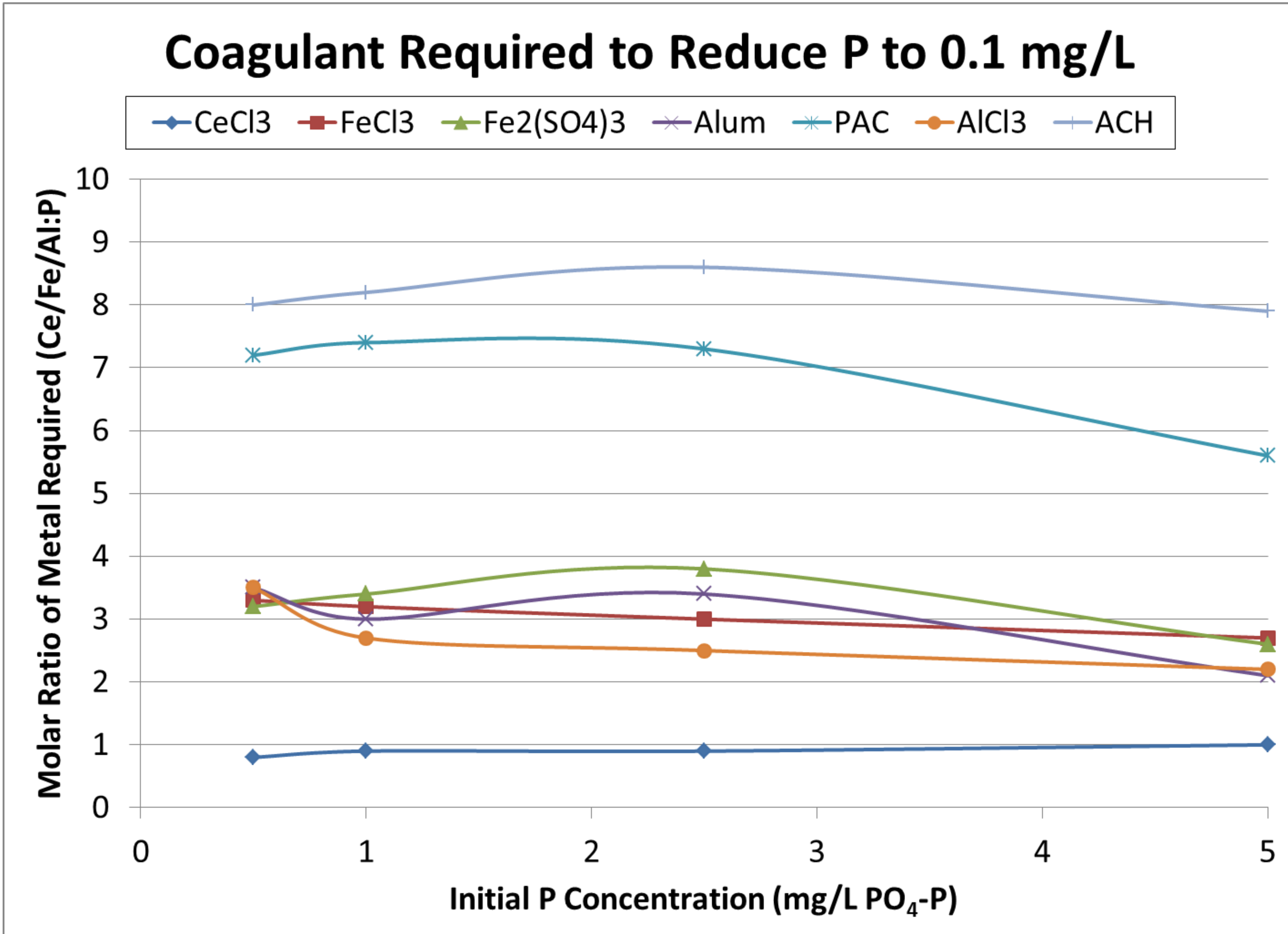
# Coagulant Comparison – 2.5 mg/L



# Coagulant Comparison – 1 mg/L



# Coagulant Comparison – Varying Initial P



## Rare Earth Performance Unaffected by Temperature

| Temperature (°C) | Molar Ratio REE:P | $RECl_3$ Dosage ($ppm_v$) |
|---|---|---|
| 5 | 0.83 | 7 |
| 20 | 0.80 | 7 |
| 40 | 0.85 | 7 |

# Effluent Toxicity Testing

- Sample tested: Secondary clarifier effluent
- Phosphorus Level: Spiked to 2 mg/L $PO_4$-P using $NaH_2PO_4$
- Treated with $CeCl_3$ at volumetric dose rate of 50 $ppm_v$
- Filtered and unfiltered samples submitted for acute whole effluent toxicity testing

| | Water Flea | | Fathead Minnow | |
|---|---|---|---|---|
| | Filtered | Unfiltered | Filtered | Unfiltered |
| **NOEC Value** | 100 | 100 | 100 | 100 |
| **$LC_{50}$ Value** | >100 | >100 | >100 | >100 |
| **$TU_a$ Value** | < 1.0 | < 1.0 | < 1.0 | < 1.0 |

## California Waste Extraction Testing

- Samples Tested:
  - Secondary clarifier effluent (spiked to 2 mg/L $PO_4$-P)
  - Centrifuge centrate (117 mg/L $PO_4$-P)
- Treated with $CeCl_3$ at dose rates of:
  - 50 $ppm_v$ for secondary clarifier effluent
  - 3,000 $ppm_v$ for centrifuge centrate
- Unfiltered samples submitted for extraction testing via CalWET procedures

# California Waste Extraction Testing

| Contaminants | Secondary Clarifier Effluent | Centrifuge Centrate |
|---|---|---|
| **Fluoride** | 0.91 mg/L | 1.5 mg/L |
| **Inorganics: Sb, As, Ba, Be, Cd, Total Cr, Hex. Cr, Co, Cu, Pb, Hg, Mo, Ni, Se, Ag, Tl, V, Zn** | BDL | BDL |
| **Pesticides** | BDL | BDL |
| **Polychlorinated Biphenyls** | BDL | BDL |
| **Herbicides** | BDL | BDL |
| **Volatiles** | BDL | BDL |
| **Bases/Neutrals/Acids (Semi-volatiles)** | BDL | BDL |

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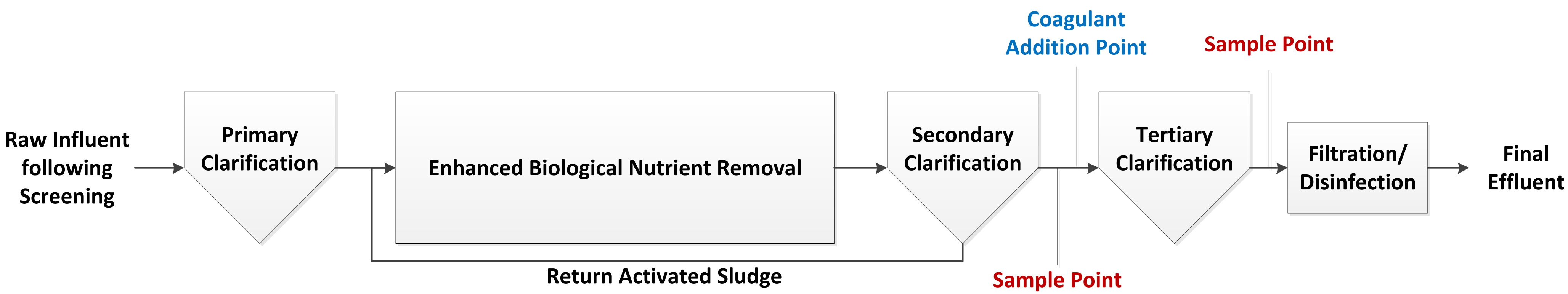
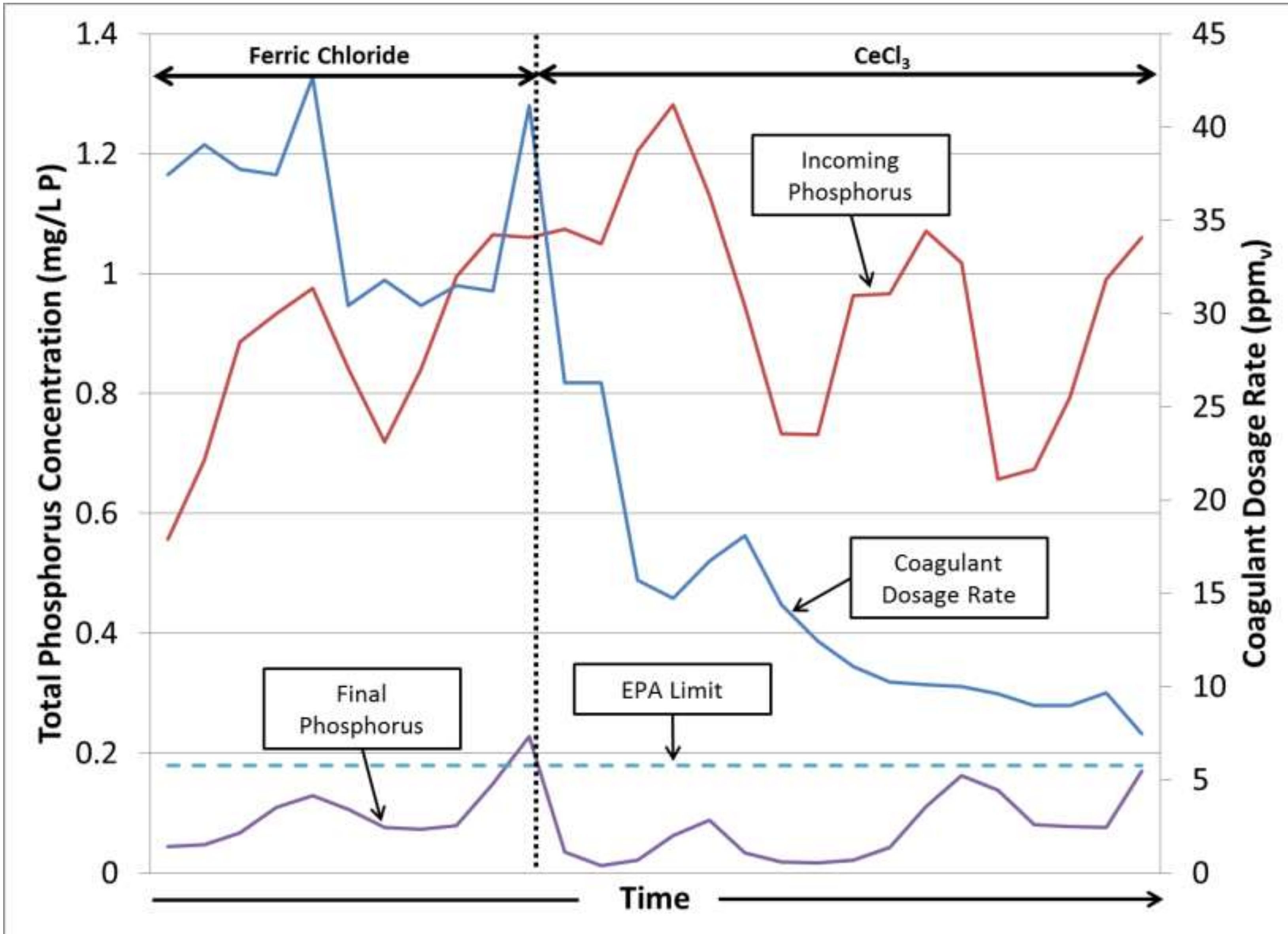
# Field Trials – Equipment Set-up

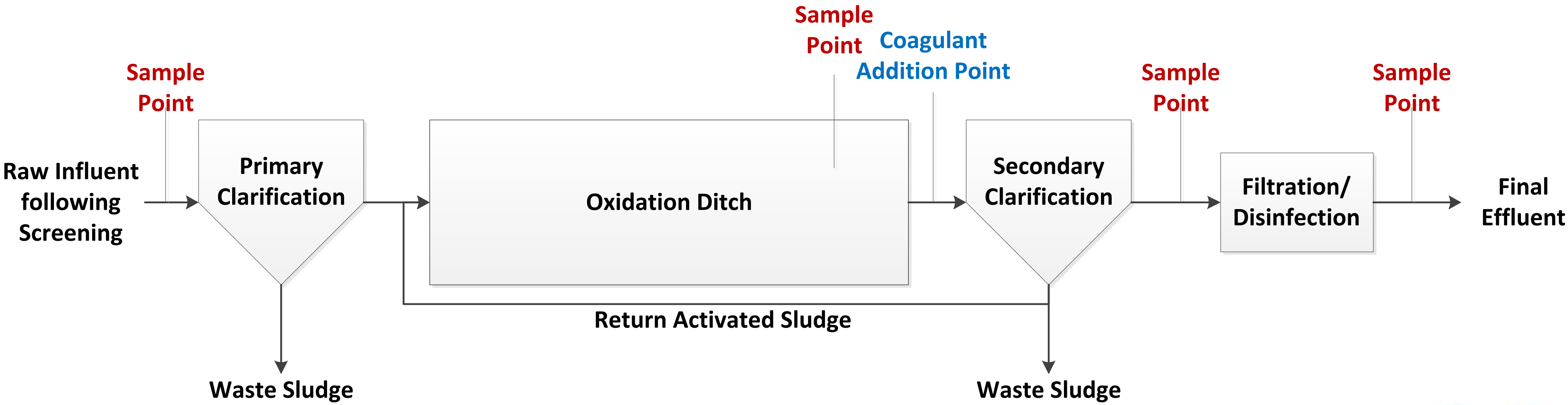
- 45 MGD municipal WWTP in Mid-Atlantic US
- Total phosphorus limit of 0.18 mg/L P
  - Target of 0.10 mg/L P
- Interested in seeking new coagulant with lower consumption rate, less chemical solids produced, and less staining of UV



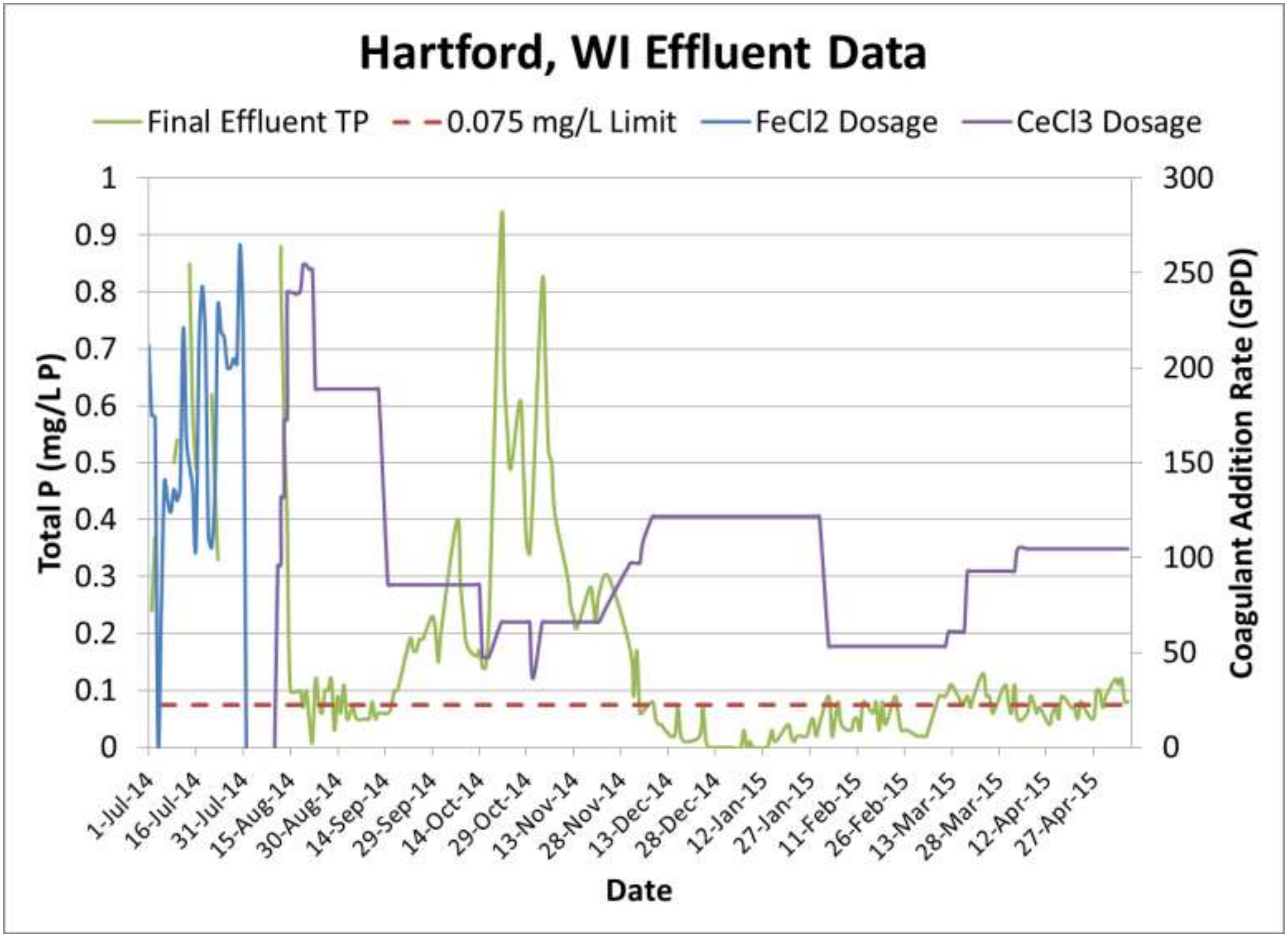
- $CeCl_3$ maintained phosphorus below limit with dosage rate 3x less than $FeCl_3$
- Ferric usage: 34 $ppm_v$ = molar ratio 3.4:1 Fe/P
- $CeCl_3$ usage: 11 $ppm_v$ = molar ratio 0.7:1 Ce/P



- 2 MGD municipal WWTF located in Wisconsin
- Total P limit of 1.0 mg/L
  - New limit of 0.075 mg/L being enacted
- Used ferrous chloride ($FeCl_2$) for chemical P removal
- Was unable to meet new TP limits with iron coagulant

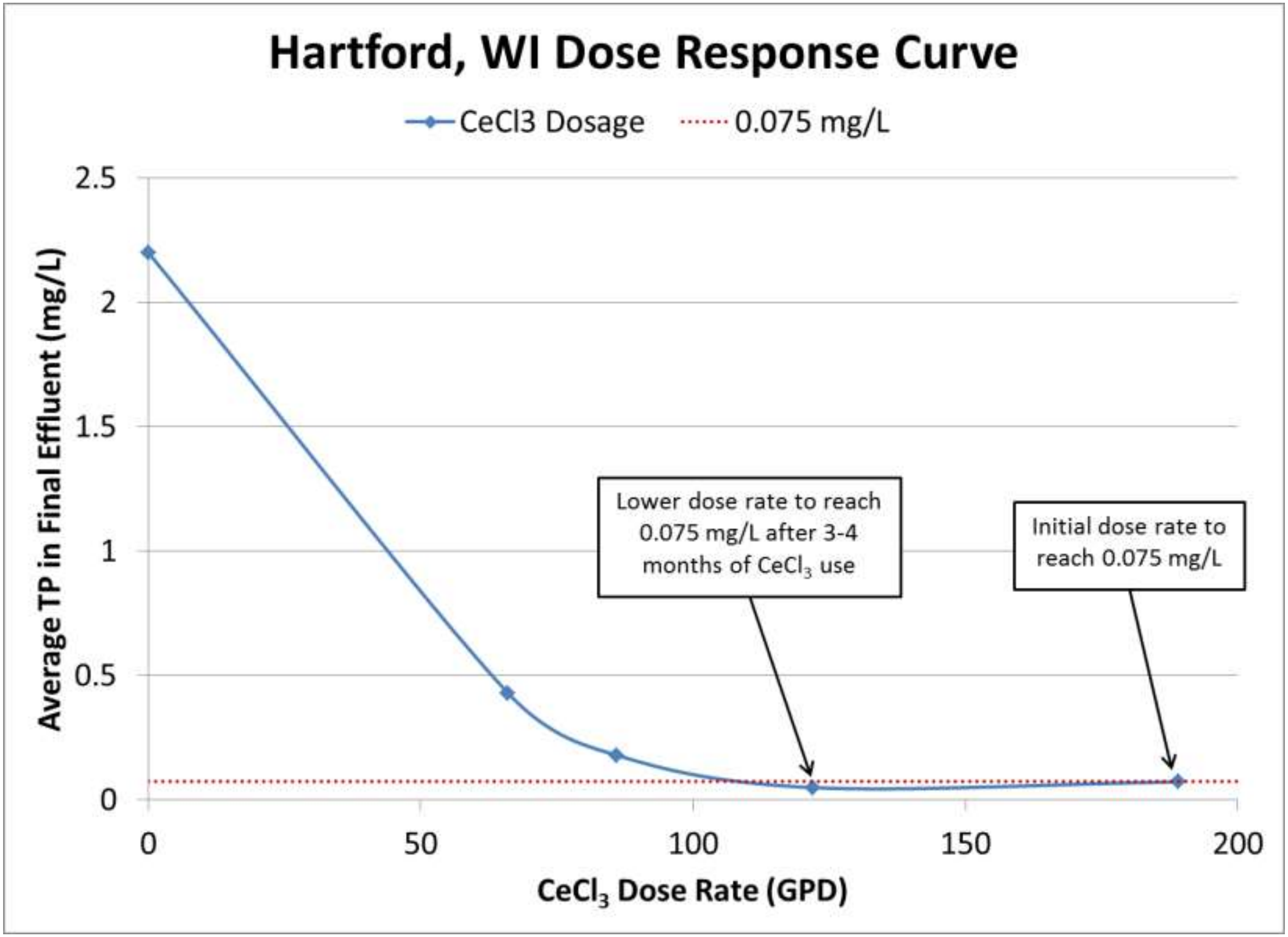


# Hartford achieved < 0.03 mg/L effluent

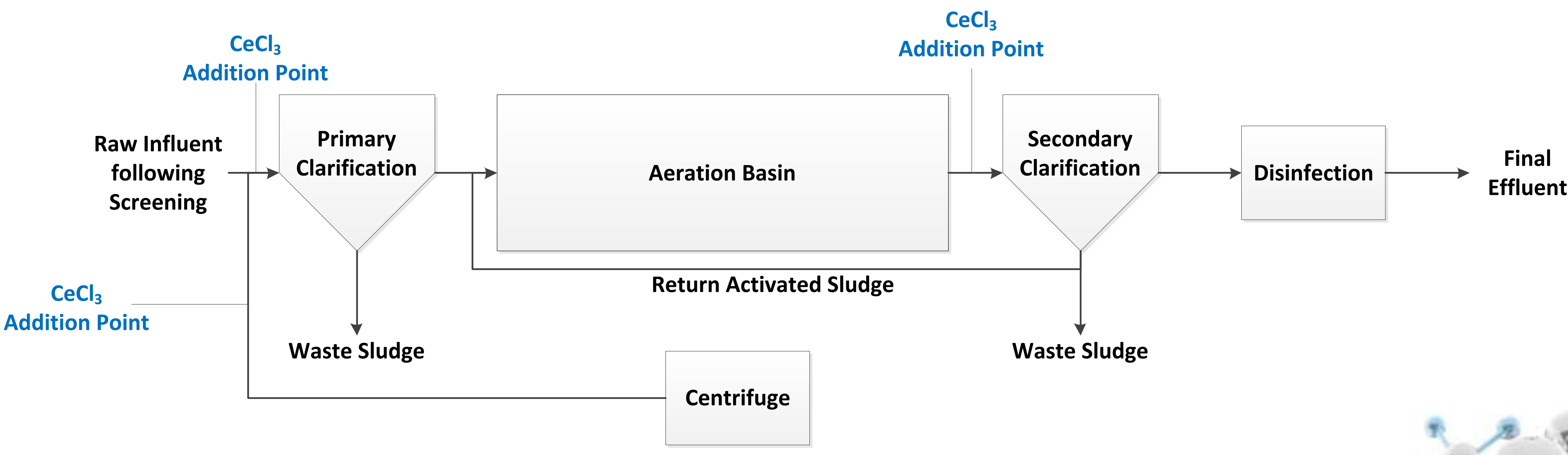



- $CeCl_3$ maintaining ave. effluent TP < 0.03 mg/L with dose rate of 120 GPD
- Historical ferrous usage required 125-250 and only reduced TP to ave. of 0.5 mg/L

# City of Hartford, WI – Dosage Curve



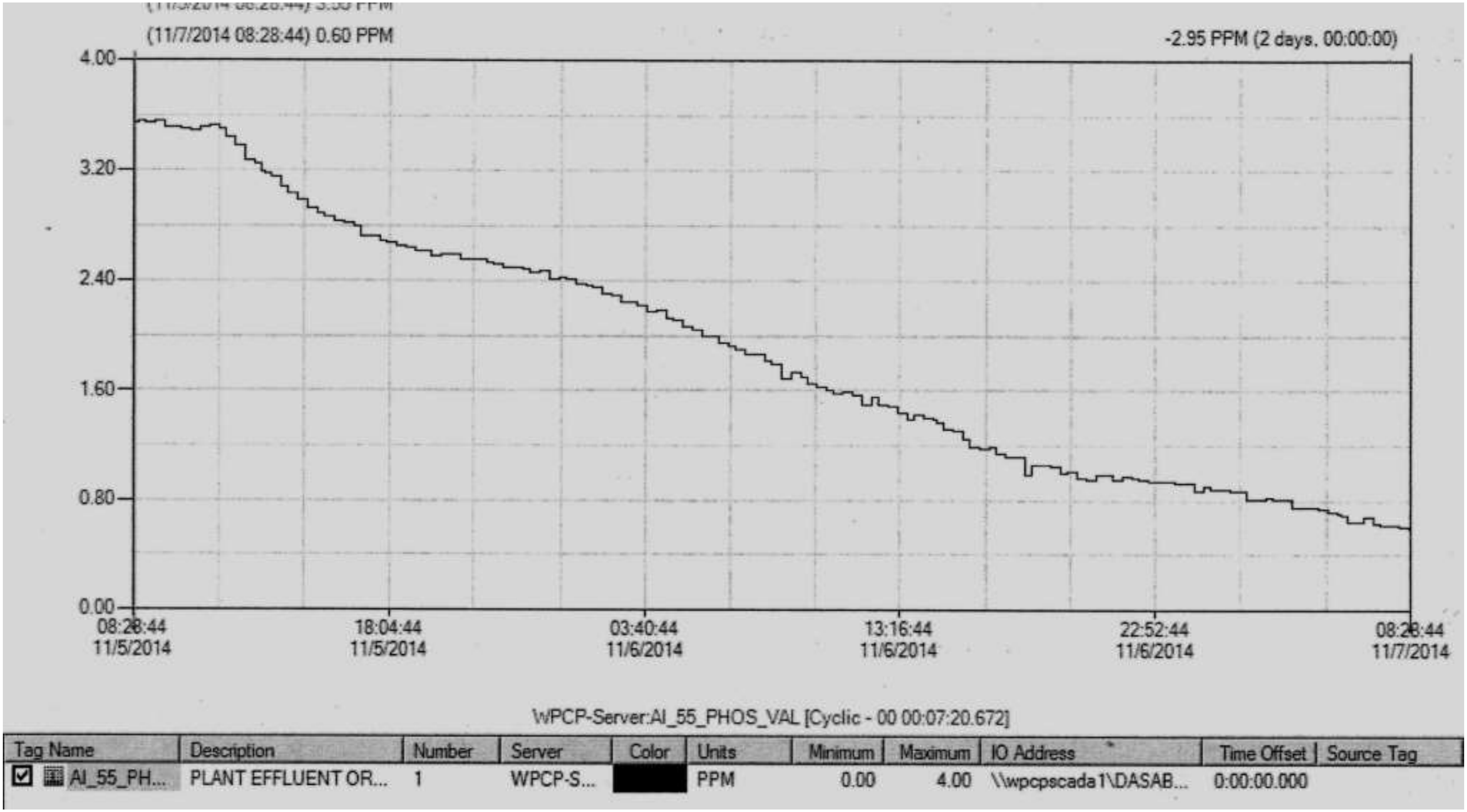
- 6-8 MGD municipal WWTF located in Wisconsin
- Total P limit of 1.0 mg/L
  - Future permit as low as 0.04 mg/L TP
- Used aluminum sulfate ($Al_2(SO_4)_3$) for chemical P removal
- Unable to meet new TP limits with alum



## Mixed Liquor sample - settling

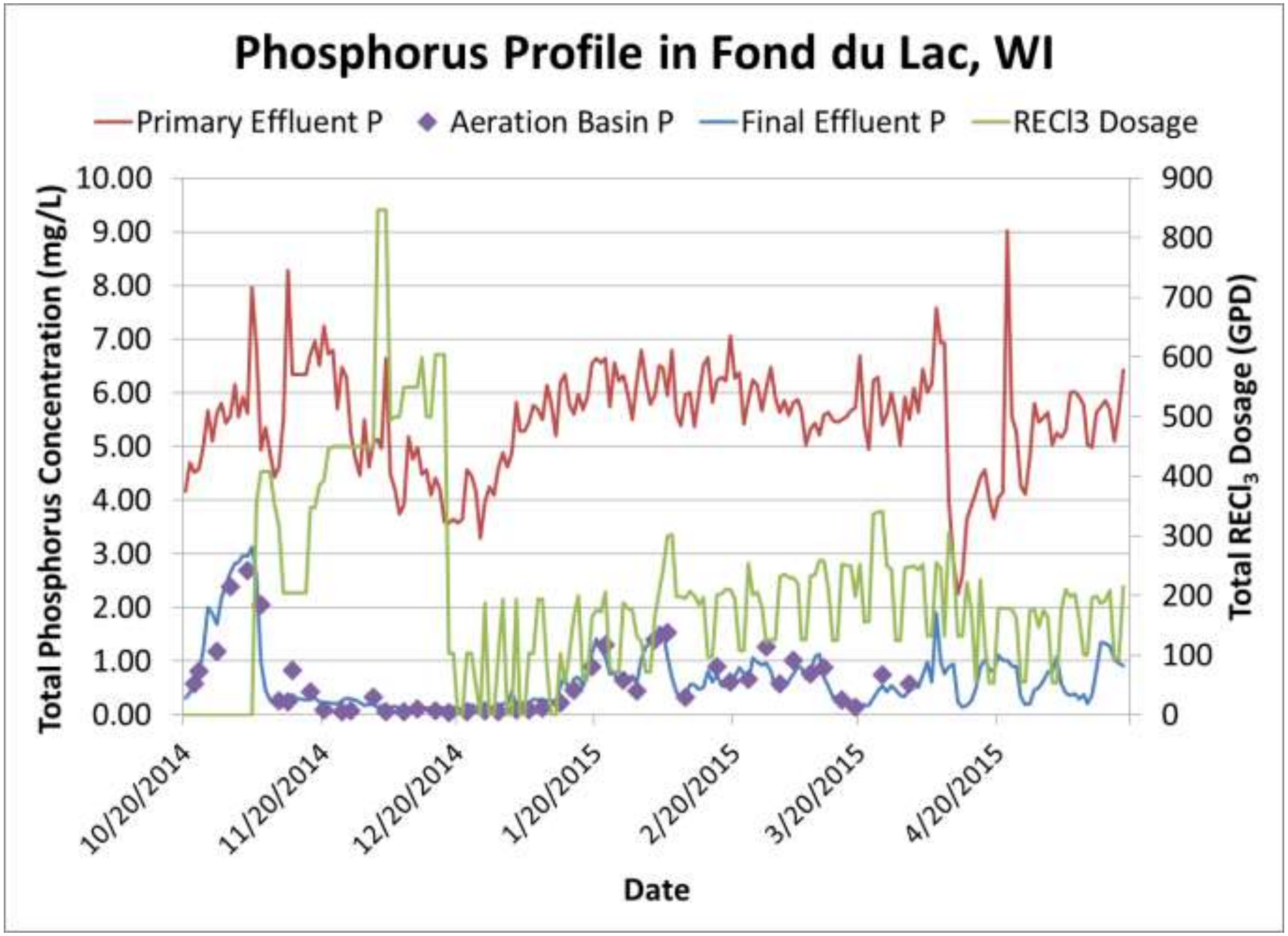
Initial 1 min 2 min 4 min 5 min 10 min

# Fast Response Time



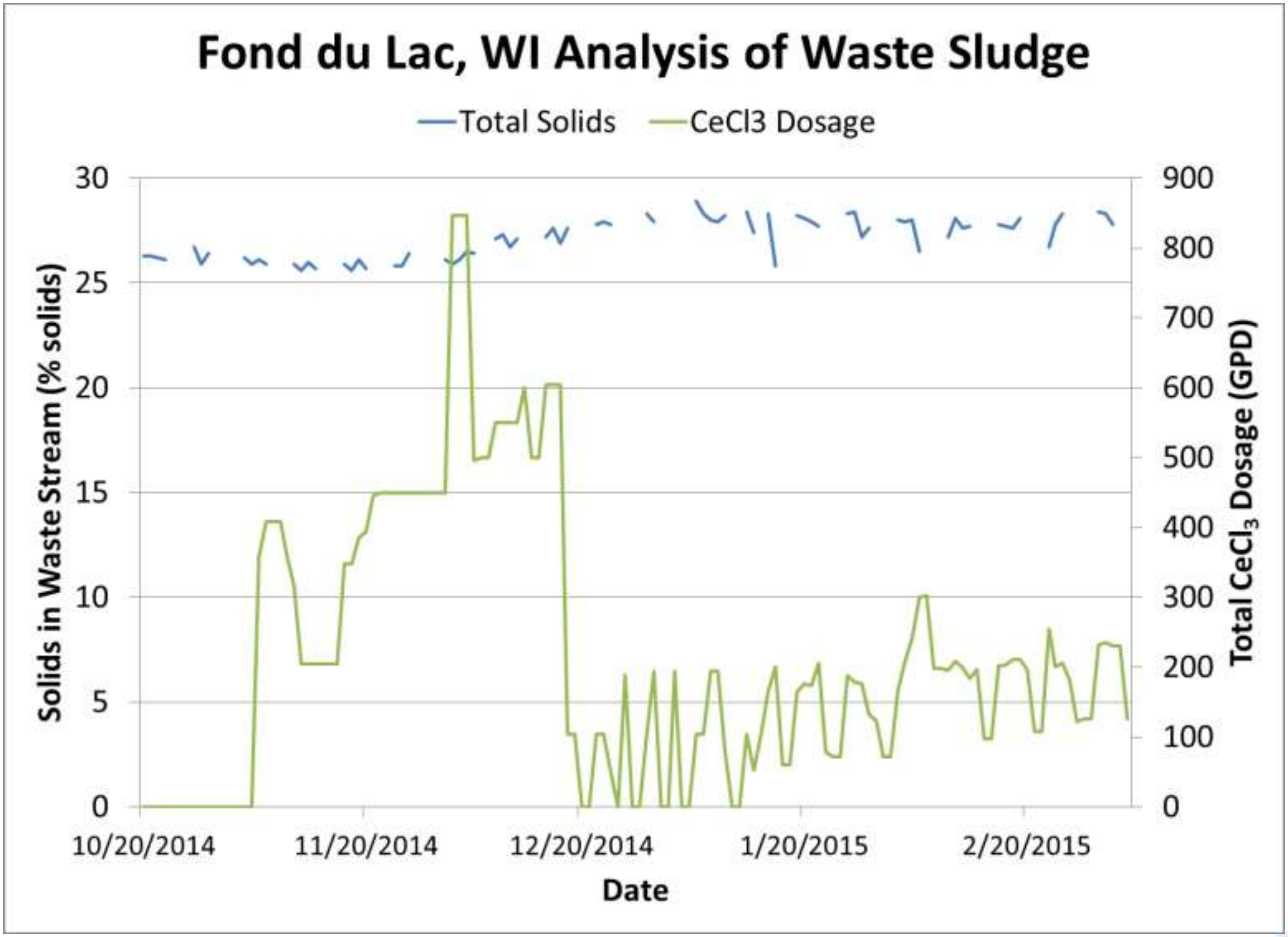

Plant Effluent – from 3.6 mg/L-PO4 to 0.6 mg/L-PO4 in 48 hours

# City of Fond du Lac, WI Results




- Achieved average of 0.15 mg/L TP in effluent for month of December with average of 50 $ppm_v$ $RECl_3$ dose
- Maintained average effluent TP at 0.6 mg/L with 200 GPD of $RECl_3$ compared to historical dose of about 700 GPD total chemical dose

- Average final sludge total solids increased from 25% to 29%



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Observed Benefits of Rare Earth Technology

- ✓ Able to achieve very low TP discharge limits without capital equipment
- ✓ Reduced sludge volumes compared to competitive coagulants
- ✓ Faster coagulation and noticeable impact than competitive coagulants
- ✓ Less coagulant volume required to reach low phosphorus limits
- ✓ Improved water clarity due to good coagulation properties
- ✓ Will not stain or discolor facility structures or equipment
- ✓ Compatible with existing dosing and filtration equipment
- ✓ Rated non-hazardous for DOT regulations

# Acknowledgements


- City of Hartford, WI WWTP - Dave Piquett
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# Questions?

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