Phosphorus: Crossover Chemical for Water Supply Impacts Wastewater

Rick Mealy, Program Chemist (DNR Certification Services)
We interrupt this session for an important disclaimer.

The speaker is not a corrosion chemistry expert. We know the effects of phosphorus on our waters. This talk focuses on its effects in drinking water.
Time to Change our Phosphorus Focus

We get so caught up in the impact of the Phosphorus Rule and non-point sources, that sometimes we have to pause and consider that to a small extent we create part of our own problem.

Granted, it’s a necessary evil, as we were reminded by the Flint Michigan crisis.

Many communities actually ADD phosphorus to their water supplies to prevent corrosion or to minimize staining from iron/manganese.

Phosphorus does play a critical role in many aspects of drinking water treatment.
Studies indicate that phosphorus found in waste water discharge only accounts for 20% of phosphorus found in our lakes and rivers.

Phosphorus from municipal drinking water contributes only about 2-10% of the phosphorus that ends up in WWTFs.
Time to change the focus...
Chemical additions is part of water supply treatment. It includes phosphates, fluoride, and chlorine. Interestingly enough, this monitoring is **NOT required to be done by a certified lab.**
The many impacts of Phosphorus

Disinfection

Corrosion Control

Fluoride

Sequester Fe/Mn
• Public water supplies (PWS) add phosphates as a corrosion inhibitor.

• Orthophosphate reacts with dissolved metals (e.g. Ca, Mg, Zn, Al etc.) in the water to form a “passivation layer” of protective coating.

• Coating keeps corrosion elements in water from attacking the pipe, limiting lead and copper release.

• If water chemistry isn’t optimized, passivation layer may start to dissolve, or flake off the pipe’s crust, exposing bare metal, and allowing iron, lead, or copper to oxidize and leach into water supply.
"I was stunned when I found out they did not have corrosion control in place. In my head, I didn't believe that. I thought: That can't be true...that's so basic."

--- EPA Water expert in a June 2016 memorandum
As the mineral layer in iron pipes falls off, it exposes bare iron that can reduce free chlorine added to the water as a pathogen-killing disinfectant.

Most important, the treated Flint River water lacked one chemical that the treated Detroit water had: phosphate.

“They essentially lost something that was protecting them against high lead concentrations,”
While phosphates work well to reduce lead solubility, copper solubility is not significantly affected by phosphate inhibitors at reasonable dosages.

The pH range at which orthophosphate is most effective for minimizing lead solubility is 7.4 to 7.8.

Unfortunately, at this pH range, chlorine added for disinfection is not as effective.

Above pH 7.8, metal phosphate precipitation can become problematic.

These interactions represent an orthophosphate demand, which reduces the amount of orthophosphate available to complex with lead.
How Flint spiraled out of control

T+30 d: Odor and color complaints. Flint R. is 70 % harder than its previous water source.

T+4 mos: Boil advisory issued due to high fecal counts. Boosted Chlorine level

T+ 5 mo: 2nd boil advisory as another failed fecals test. Virginia Tech finds Flint R water is 12-19 times more corrosive than L. Huron source water.

T+6 mo: GM stops using Flint R water; concerns for corrosion in its machines and engine blocks.

T+9Mo: Flint found to be in violation of the SDWA due to excessive TTHM levels in the water

T+10 mo: 1st residential Pb test shows 5X EPA MCL

T+1 yr: Official notice that corrosion control plan not implemented
A view of Flint drinking water pipes, showing different kinds of iron corrosion and rust.

Source: FlintWaterStudy.org
lead pipe  corroded steel pipe  lead pipe treated with oPO4

Credit: U.S. EPA Region 5
### Moving from Health to Aesthetics

#### Secondary Drinking Water Standards (ug/L)

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Secondary MCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>300</td>
</tr>
<tr>
<td>Manganese</td>
<td>50</td>
</tr>
</tbody>
</table>
Neither iron nor manganese in water present a health hazard.

Aesthetically, however, they may cause taste, staining, and accumulation problems.

Iron will cause reddish-brown staining of laundry, porcelain, dishes, utensils, and even glassware.

Manganese characterized by brownish-black stain.

Soaps & detergents don’t remove these stains, use of chlorine bleach can actually intensify staining.

They come as a package deal: typically if you have Fe, you have Mn as well.
Aesthetics of Iron & Manganese

Iron Staining

Iron & Manganese Staining
What is sequestering?

1. Take us to your Iron!

Polyphosphates out-compete oxygen for the iron

Oxygen + iron = iron oxides = red stains

NO! We shall keep Fe in solution

I’m off to stain the laundry!!!
Why sequester?

Polyphosphates react with soluble metals (Fe, Mn, Ca, Mg, etc.) by sequestering (binding-up) the metals to maintain their solubility in water.

Reduces discoloration, staining, scaling, chlorine demand, taste/odor and other aesthetic concerns.

If phosphates are not binding minerals before they come into contact with the chlorine, unsequestered Fe and Mn will oxidize and precipitate from solution.

Increasing phosphate levels will not sequester previously oxidized minerals that have flocculated together or are precipitating from solution.
**Blended phosphate technology** has proven to be a cost effective means of treating drinking water systems.

Successful treatment levels are usually **1.0 to 2.0 ppm**.

Blending provides a tenacious protective coating at the cathodic and anodic sites.

Key is in blending in a variety of polyphosphate compounds.

Polyphosphates provide a scrubbing action on the metal surfaces limiting the amount of protective coating deposited.

Blending provides a strong protective film while scrubbing away old deposits and biofilm formations.
For this talk, let’s agree to avoid discussions related to the allegation that fluoride additions represent forced government mass medication on the populace 😊
Fluoridation IS controversial.

"Water contains a number of substances that are undesirable, and fluorides are just one of them."

Dr. F. A. Bull, State Dental Director

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Relative Toxicity

- Lead
- Fluoride
- Arsenic

EPA Maximum Contaminant Levels

- Lead
- Fluoride
- Arsenic

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"public health officials have often suppressed legitimate scientific doubts in order to reassure the public."
- Oakland Tribune

"Effects of ingested fluoride is not within the purview of dentistry."
- California Board of Dental Examiners

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For example, if you have cereal with milk and a Coke, you have overdosed on fluoride. You have exceeded the American Dental Association’s recommended daily dose.
Most small systems will use a colorimeter for their required fluoride monitoring. Referenced methods state that phosphate levels above 16 mg/L (as PO₄) will interfere.

### Hach

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Concentration</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate, ortho</td>
<td>16 mg/L</td>
<td>+0.1 mg/L F⁻</td>
</tr>
</tbody>
</table>

**mg/L Error at 1.0 mg F⁻/L in Fluoride Methods**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Conc. mg/L</th>
<th>Type of Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexametaphosphate ([NaPO₃]₆)</td>
<td>1.0</td>
<td>+</td>
</tr>
<tr>
<td>Phosphate (PO₄³⁻)</td>
<td>16</td>
<td>+</td>
</tr>
</tbody>
</table>

aka: Polyphosphate
So we did a little test of our own...

What do you believe? Methods...or hard data? Methods that are ancient, have not been updated and been copied by others as is?

<table>
<thead>
<tr>
<th>Ortho-phosphate (mg/L PO4)</th>
<th>True F- (mg/L)</th>
<th>Measured F- with SPADNS (mg/L)</th>
<th>Measured F- with ISE (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>1.00</td>
<td>1.01</td>
</tr>
<tr>
<td>0.5</td>
<td>1.00</td>
<td>1.30</td>
<td>1.01</td>
</tr>
<tr>
<td>1.0</td>
<td>1.00</td>
<td>1.55</td>
<td>1.02</td>
</tr>
<tr>
<td>1.5</td>
<td>1.00</td>
<td>1.65</td>
<td>1.00</td>
</tr>
</tbody>
</table>
## Bonus info: Temp. Effects on Fluoride

<table>
<thead>
<tr>
<th>Temperature Degrees Centigrade</th>
<th>True Fluoride mg/L</th>
<th>Measured fluoride SPADNS mg/L</th>
<th>Measured fluoride ISE mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 (39°F)</td>
<td>1.0</td>
<td>1.5</td>
<td>1.14*</td>
</tr>
<tr>
<td>10 (50°F)</td>
<td>1.0</td>
<td>1.5</td>
<td>1.27*</td>
</tr>
<tr>
<td>20 (69°F)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* drifting problems
Bottom Line: Phosphate being fed into water supplies can create a high bias in fluoride testing.

Note also, that there is low bias in fluoride results when the water tested is cold.

Low bias could lead to facilities RAISING the fluoride dosage which may exceed levels for positive dental benefits.

All PWS that add fluoride are required to monitor fluoride levels daily and submit a split sample –by statute– to the State Lab of Hygiene monthly. This split sample is required BECAUSE of the known biases in fluoride testing.

...and remember... fluoride monitoring for chemical additions is NOT required to be done by a certified lab!
Phosphorus & Disinfection (Chlorine)
• Wisconsin does not require utilities to disinfect their water to eliminate pathogens, *though federal regulations do require those using surface water to disinfect*. 

  – In 2009, the DNR began promoting new state regulations to require universal disinfection,

  – In 2011, the Legislature struck those rules.

• Only 56 municipal water utilities in Wisconsin do not disinfect their water. Serve slightly > 1% of the state's population (*almost 65,000 people*).
Biofilm micro-organisms use phosphorus and carbon piping, secrete acidic enzymes that dissolve metal, and result in pit corrosion.

Studies have shown that addition of phosphates has extended survival of E. coli in distribution system.

If pipe surface is over-exposed, chlorine is used up oxidizing Fe/metals while releasing Pb.

If you have nutrients and poor disinfection, you will have biological growth and likely microbial induced corrosion (MIC).

In addition, adding PO4 raises the pH a bit, which reduces disinfection efficiency.
The phosphate feed point should be ahead of the chlorine injection point.

If phosphate is fed after chlorine, there is a possibility the iron and manganese will be oxidized by the chlorine before sequestering can take place.

This will result in iron and manganese precipitates to be pumped out into the distribution system.

Plus ...you lose disinfection power!!!
Many labs just rinse sample carboys with tap water.

But...if the tap water contains phosphate additives...

You are adding phosphorus background!!!

...which will impact LODs determined by the new LOD protocol promulgated by the EPA.

And also remember that Alconox is 8.7% phosphorus!

**Remember:**

Total P (mg/l as P) x 3.065 = PO4

PO4 (mg/l as PO4) x 0.3262 = Total P

TP x 3 = PO4

PO4 ÷ 3 = TP
Sample Pumpage Report

<table>
<thead>
<tr>
<th>DATE</th>
<th>PUMPAGE IN</th>
<th>CHEMICAL (lbs)</th>
<th>CALCULATED DOSE (PPM)</th>
<th>RESIDUAL TEST (PPM)</th>
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<tbody>
<tr>
<td>1</td>
<td>642</td>
<td>33.00</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>844</td>
<td>40.00</td>
<td>0.90</td>
<td>0.98</td>
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<tr>
<td>3</td>
<td>748</td>
<td>40.00</td>
<td>1.02</td>
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</tr>
<tr>
<td>4</td>
<td>639</td>
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<td>5</td>
<td>424</td>
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<td>6</td>
<td>807</td>
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<tr>
<td>7</td>
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<td>1.00</td>
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<td>8</td>
<td>1151</td>
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<td>9</td>
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<td>11</td>
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<td>12</td>
<td>644</td>
<td>34.00</td>
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<tr>
<td>13</td>
<td>816</td>
<td>44.00</td>
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<td></td>
</tr>
<tr>
<td>14</td>
<td>865</td>
<td>50.00</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>751</td>
<td>44.00</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>778</td>
<td>45.00</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOT.</td>
<td></td>
<td>23617</td>
<td>1306.00</td>
<td>31.63</td>
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<tr>
<td>AVG.</td>
<td></td>
<td>787.233</td>
<td>43.53</td>
<td>1.05</td>
</tr>
</tbody>
</table>

8.34 x 1 ppm = 8.34 lbs/MGD/day
Phosphate forms play a vital role in water supply chemistry.

Inorganic phosphates are used for corrosion control (control of Pb/Cu).

Polyphosphates are used to sequester Fe/Mn.

“Blends”, containing the elements of both corrosion control and sequestering Fe/Mn are used as well.

Phosphate can cause high bias in fluoride testing.

Addition of phosphates can extend survival rates of E. coli.

Use of phosphates can also impact disinfection, which in turn can impact corrosion.
Thanks,

Rick Mealy, DNR
Richard.Mealy@Wisconsin.gov

Desk: (608) 264-6006    Cell (608) 219-6285