Phosphorus: Crossover Chemical for Water Supply Impacts Wastewater

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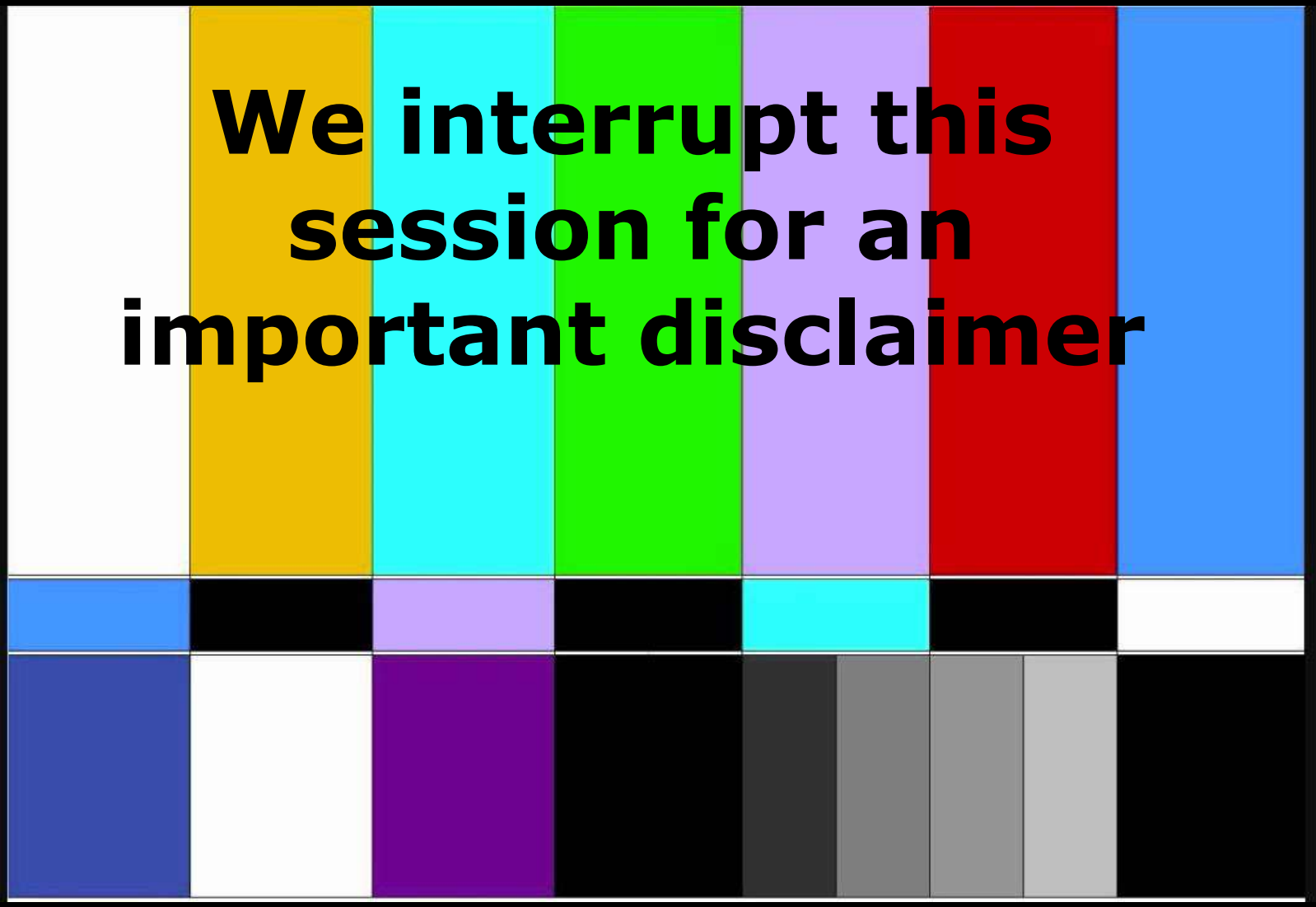
(DNR Certification Services)



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

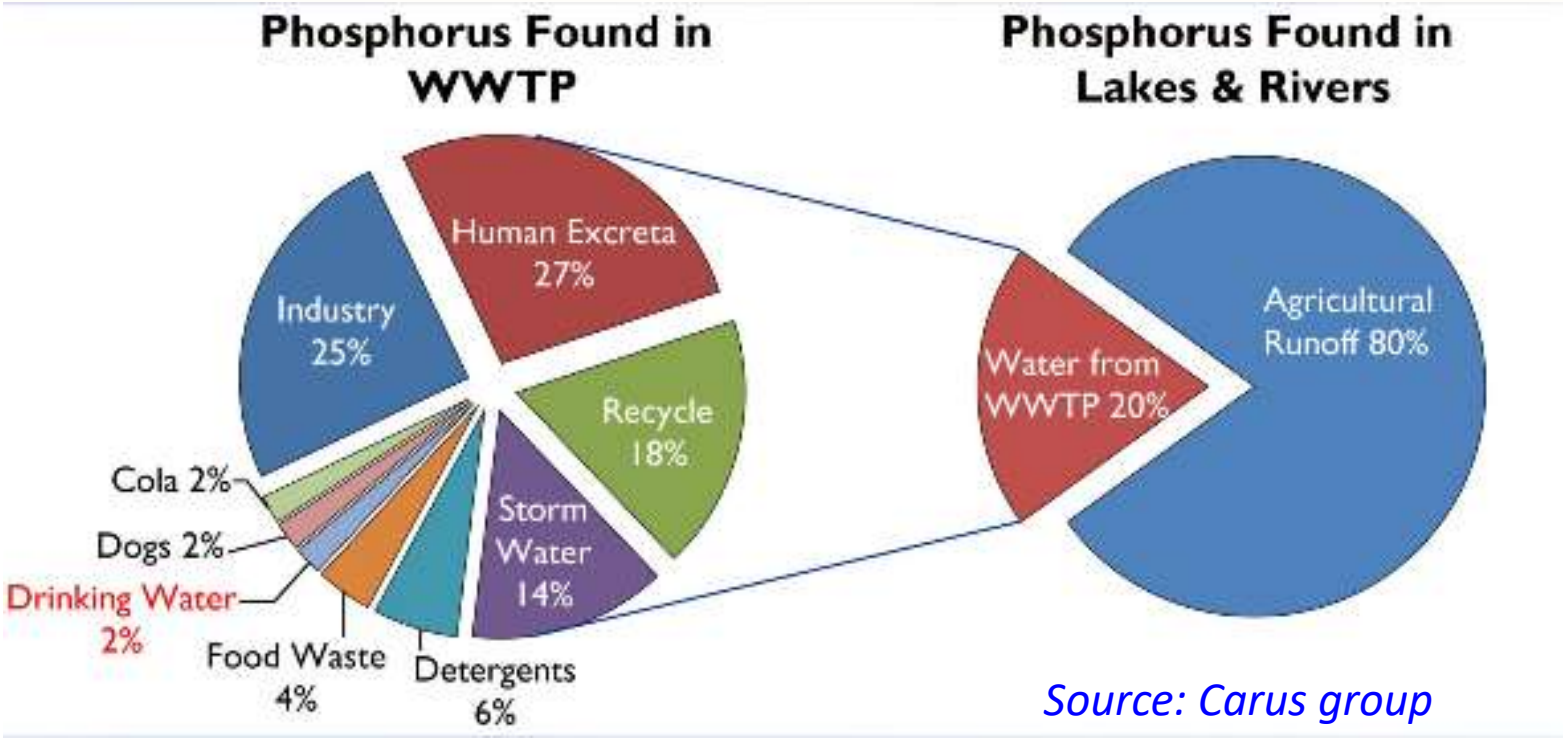
We get so caught up in the impact of the Phosphorus Rule and non-point sources, that sometimes we have to pause and consider that to a small extent we create part of our own problem.

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.

Is Water Supply P a big Problem?



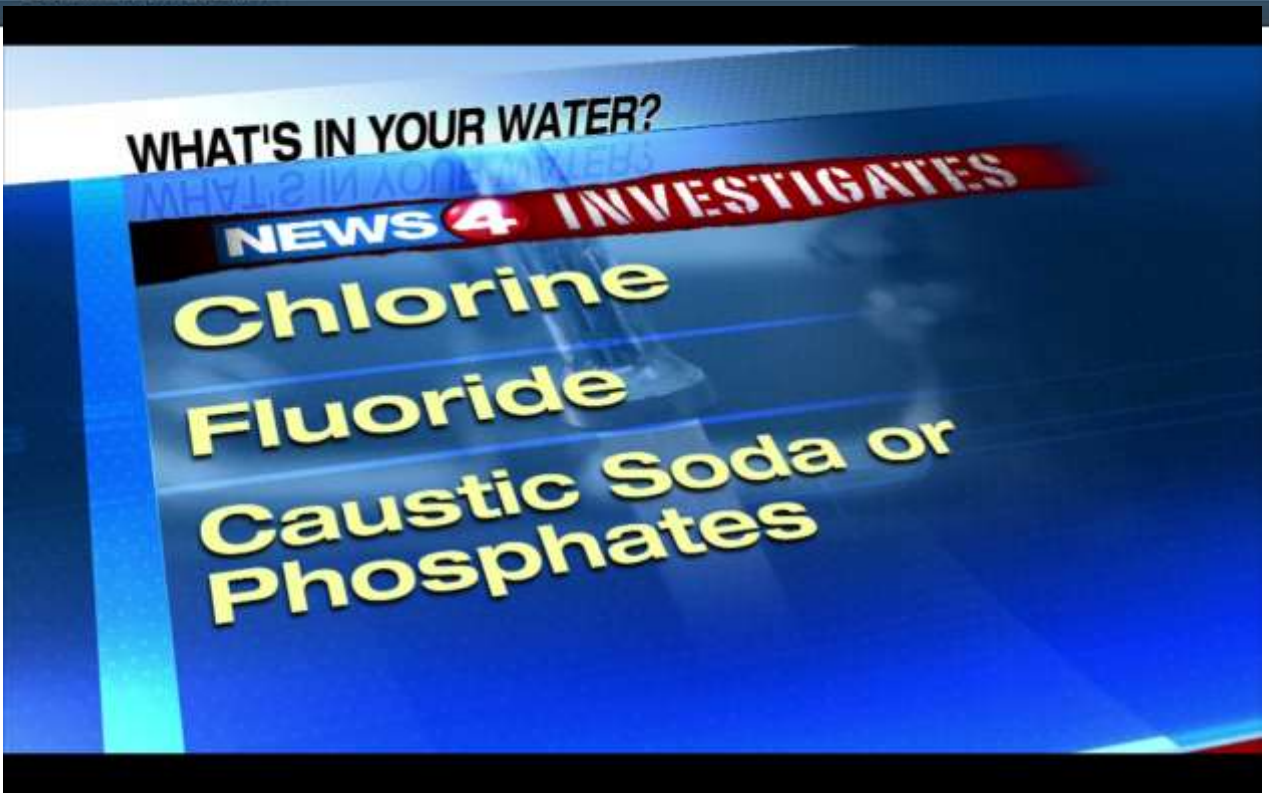
Source: Carus group

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…

…and look at drinking water



- 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

P

Fluoride

Sequester Fe/Mn

P & CORROSION CONTROL

Orthophosphate: Corrosion Control

- 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.

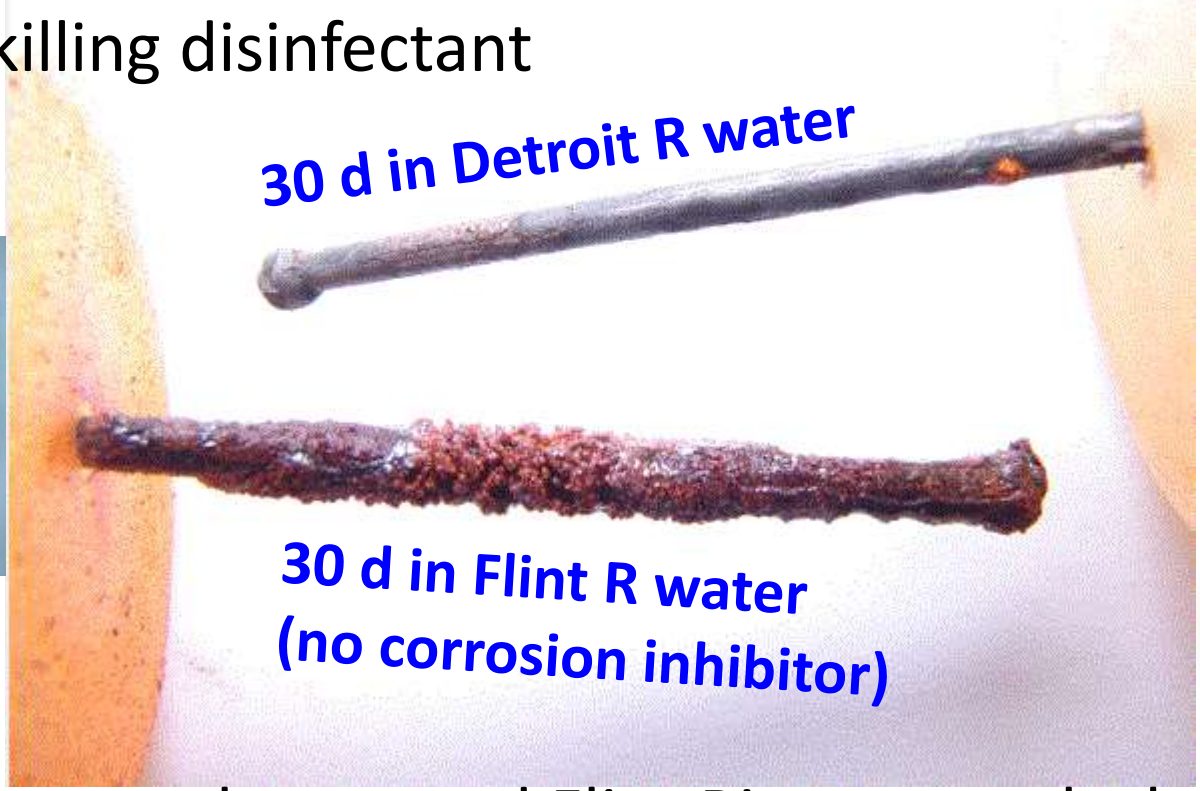
Flint Michigan Crisis

"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

How corrosive was it?

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,"

C&EN Volume 94 No.7 | 2/11/2016

Corrosion Control

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

The Science Behind It: Corrosion Caused Lead-Tainted Water in Flint, Michigan

By *Kathy Riggs Larsen* on 6/7/2016 [Materials Performance] 3:46 PM

By Associated Press | Posted: Wed 12:01 PM, Feb 10, 2016

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

Phosphorus & Sequestration

Moving from Health to Aesthetics

Secondary Drinking Water Standards (ug/L)

Contaminant	Secondary MCL
Iron	300
Manganese	50

Sequestering Fe/Mn

Iron and Manganese Problems

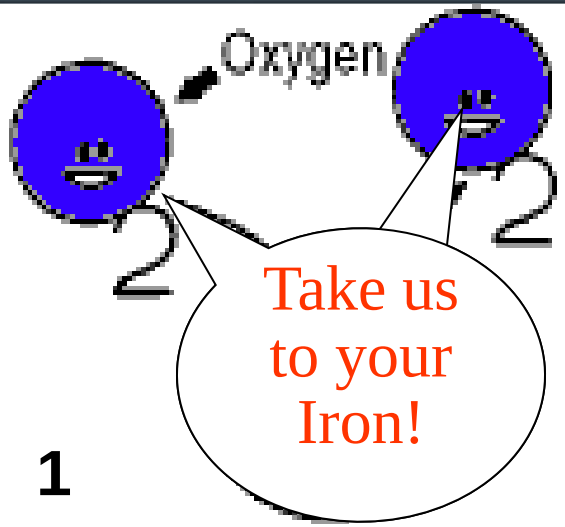
- Neither iron nor manganese in water present a health hazard.
- Aesthetically, however, they may cause taste, staining, and accumulation problems.
- Iron will cause reddish-brown staining of laundry, porcelain, dishes, utensils, and even glassware.
- Manganese characterized by brownish-black stain.
- 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?



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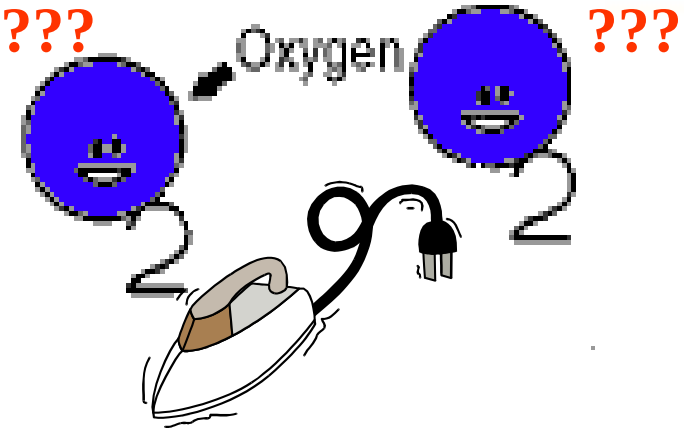
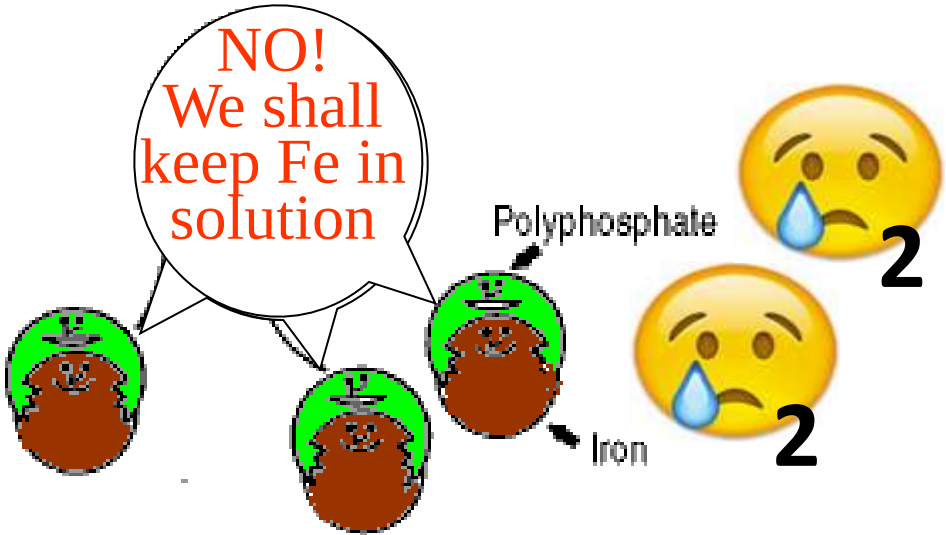


Ooops…wrong iron

2

Polyphosphates out-compete oxygen for the iron



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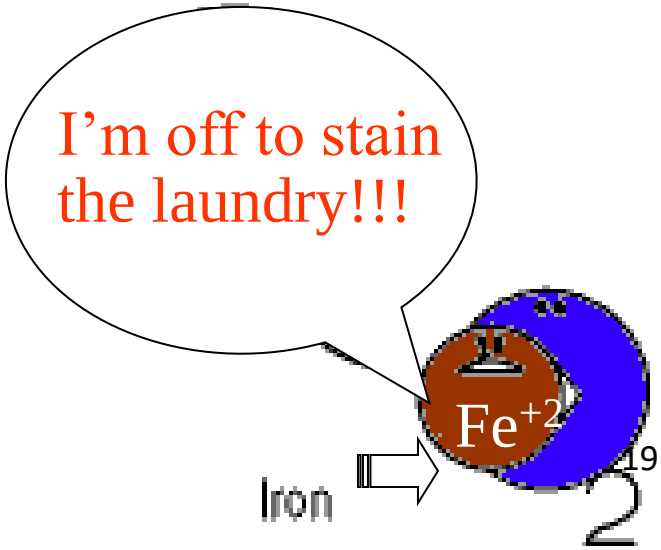
Oxygen + iron =iron oxides = red stains



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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 Phosphates

Blended phosphate technology has proven to be a cost effective means of treating drinking water systems.

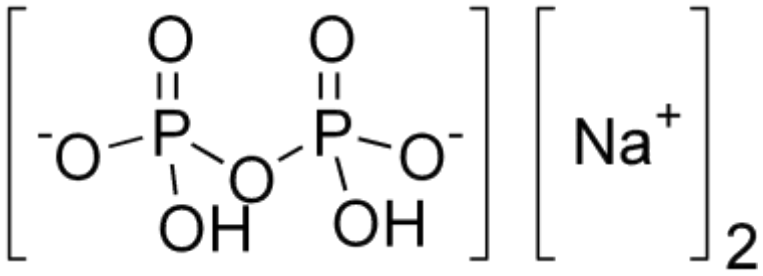
Successful treatment levels are usually 1.0 to 2.0 ppm.

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.



Phosphorus & Fluoride

For this talk, let's agree to avoid discussions related to the allegation that fluoride additions represent forced government mass medication on the populace ☺

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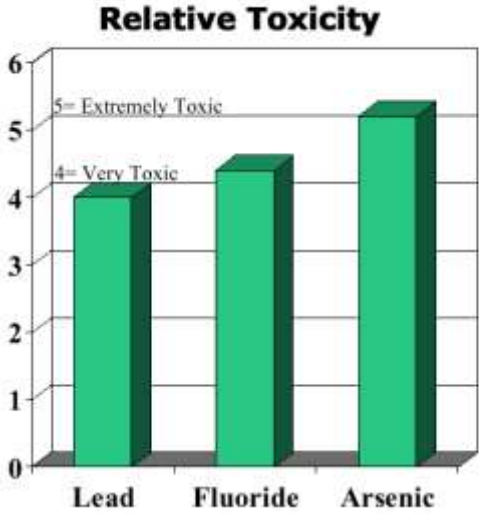
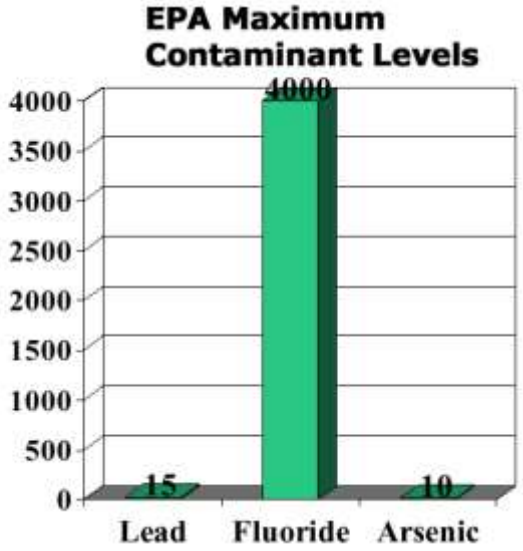
"Water contains a number of substances that are undesirable, and fluorides are just one of them"
Dr. F. A. Bull, State Dental Director





"..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

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

Bias on Fluoride testing by colorimetry

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

FLUORIDE, continued

Interferences

Substance	Concentration	Error
Phosphate, ortho	16 mg/L	+0.1 mg/L F^-

Standard Methods

MG/L ERROR AT 1.0 MG F^-/L IN FLUORIDE METHODS

Substance	Method D (SPADNS) Conc mg/L	Type of Error*
Hexametaphosphate ($[NaPO_3]_6$)	1.0	+
Phosphate (PO_4^{3-})	16	+

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?

Ortho-phosphate	True F-	Measured F- with SPADNS	Measured F- with ISE
mg/L PO4	mg/L	mg/L	mg/L
0	**1.00**	**1.00**	**1.01**
0.5	**1.00**	**1.30**	**1.01**
1.0	**1.00**	**1.55**	**1.02**
1.5	**1.00**	**1.65**	**1.00**

Bonus info: Temp. Effects on Fluoride

Temperature Degrees Centigrade	True Fluoride mg/L	Measured fluoride SPADNS mg/L	Measured fluoride ISE mg/L
4 (39°F)	1.0	1.5	1.14*
10 (50°F)	1.0	1.5	1.27*
20 (69°F)	1.0	1.0	1.0

* drifting problems

Summary: Fluoride addition

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)

Disinfection basics

- 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*).

Phosphorus & Disinfection

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.

Putting the cart before the horse

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!!!

In the WWTP lab

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 **TP x 3 = PO4**

PO4 (mg/l as PO4) x 0.3262 = Total P **PO4 ÷ 3 = TP**

8.34 x 1 ppm = 8.34 lbs/MGD/day

Sample Pumpage Report

DATE	PUMPAGE IN 1,000 GAL.	AQUAMAG CHEMICAL USED (lbs)	AQUAMAG CALCULATED DOSE (PPM)	AQUAMAG RESIDUAL TEST (PPM)
1	642	33.00	0.98	
2	844	40.00	0.90	0.98
3	748	40.00	1.02	
4	639	35.00	1.04	
5	424	20.00	0.90	0.86
6	807	43.00	1.02	
7	860	48.00	1.06	1.00
8	1151	66.00	1.09	
9	898	49.00	1.04	1.01
10	826	47.00	1.08	
11	928	52.00	1.07	
12	644	34.00	1.01	1.07
13	816	44.00	1.03	
14	865	50.00	1.10	
15	751	44.00	1.12	
16	778	45.00	1.10	
17	477	26.00	1.04	
18	941	53.00	1.07	0.31
19	633	36.00	1.08	
20	855	48.00	1.07	0.98
21	716	40.00	1.07	
22	754	42.00	1.06	
23	895	41.00	0.87	
24	627	46.00	1.40	
25	1025	56.00	1.04	1.44
26	606	34.00	1.07	
27	883	50.00	1.08	
28	1006	54.00	1.02	
29	725	42.00	1.10	
30	853	48.00	1.07	
31				
TOT.	23617	1306.00	31.63	7.65
AVG.	787.233	43.53	1.05	0.9563

Summary

- 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

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