Copper Corrosion: Copper Release to Pitting Attack

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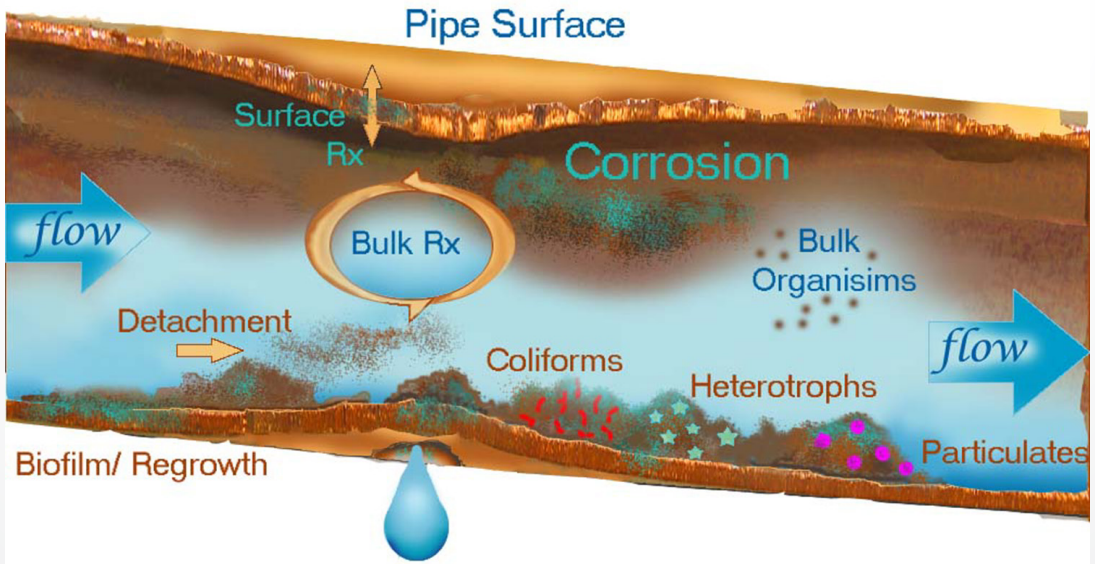
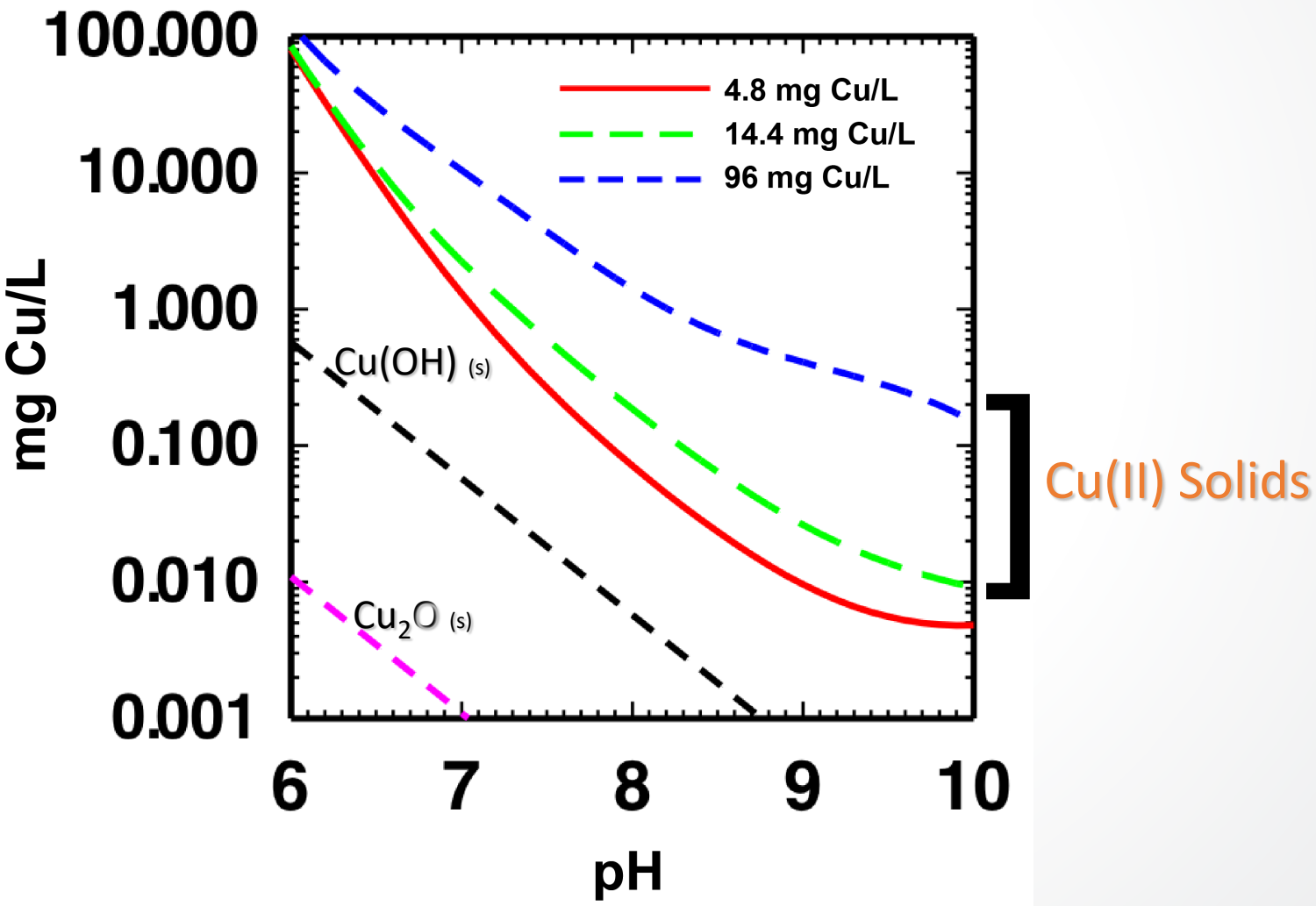
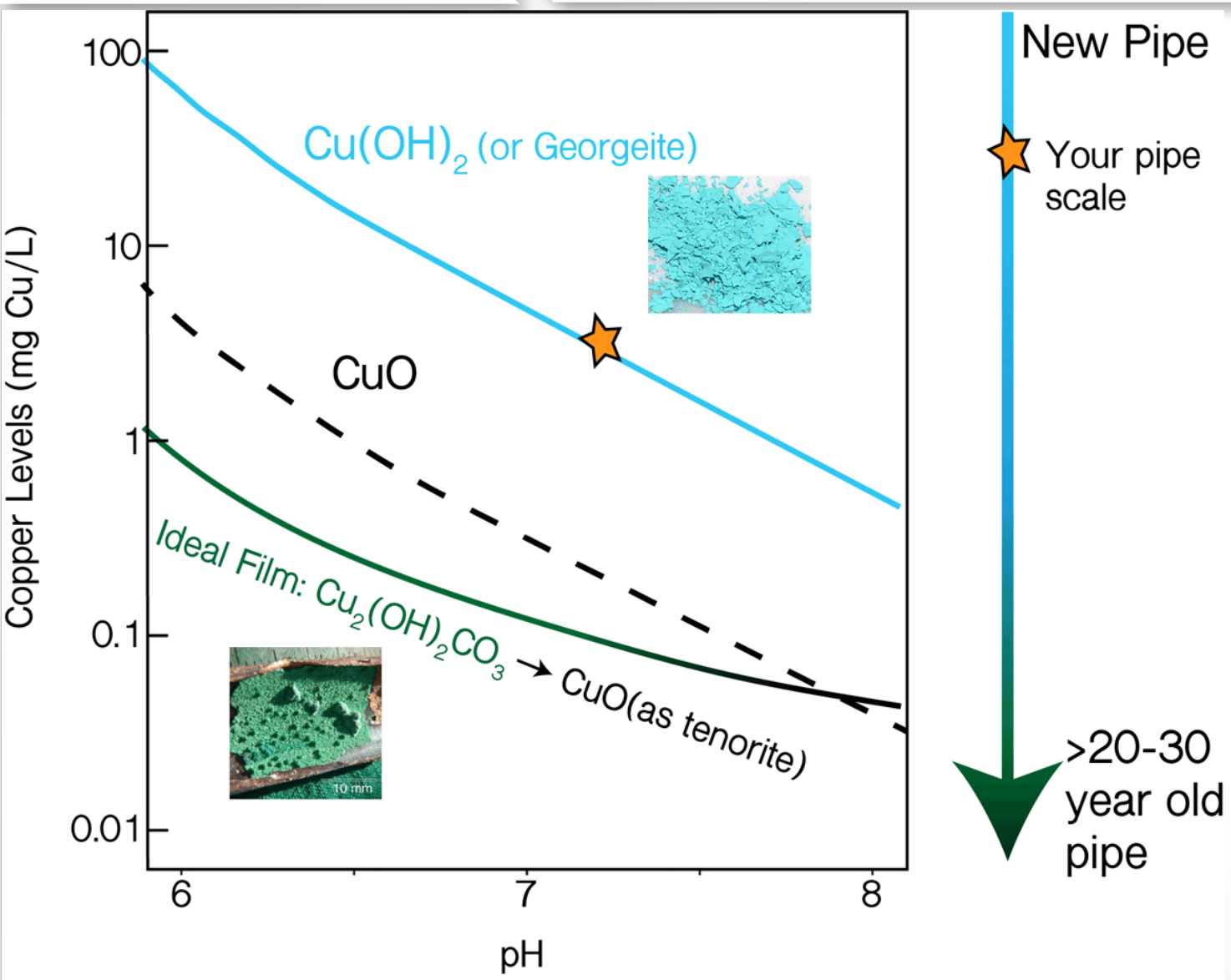


Copper(II) Solubility at Different DIC Levels Compared to Copper(I) Solubility



Evolution of Scale Model for High DIC, Low pH Waters



Theoretical Aging Process:

Recrystallizing

↓

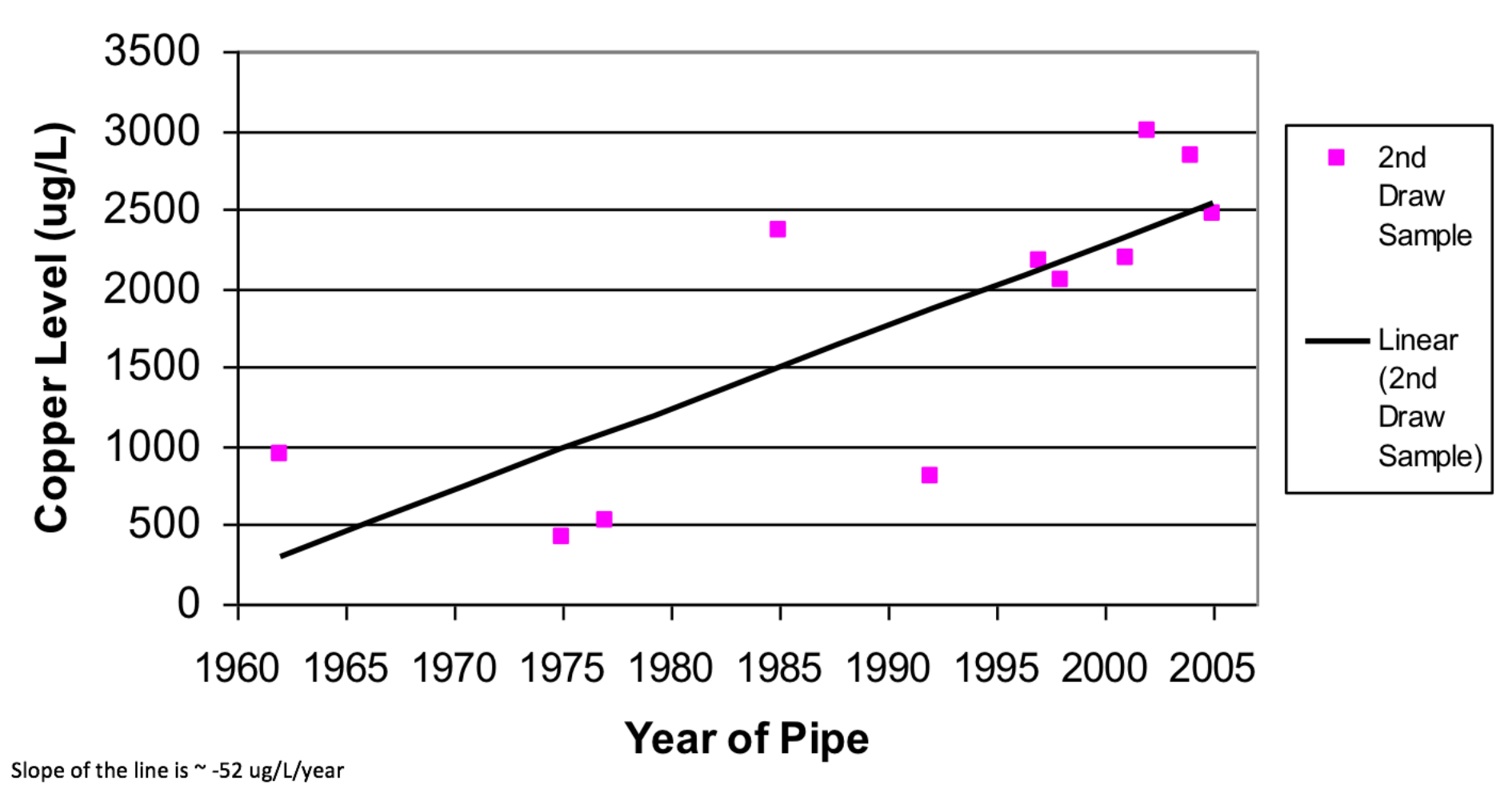
Decreasing surface area

↓

Reacting with CO_3 or HCO_3^-

Time: 20-30+ years with high DIC

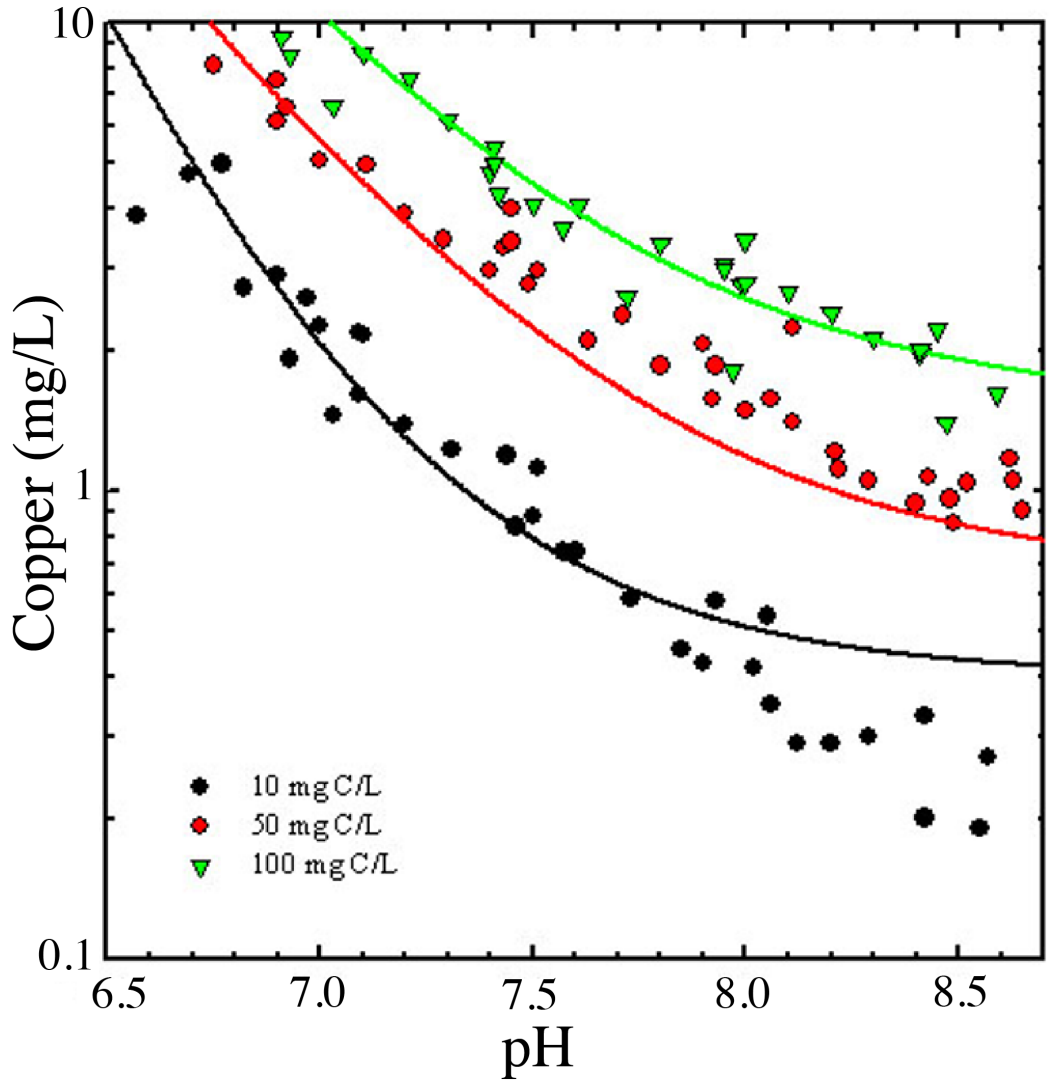
Impact of Plumbing Age on 2nd Draw Copper Concentrations



A 2nd draw sample is a 1L sample immediately following a 1st draw.

Data from M.S. Thesis of N. Turek, "Investigation of Copper Contamination and Corrosion Scale Mineralogy in Aging Drinking Water Distribution Systems", AFIT, 2006.

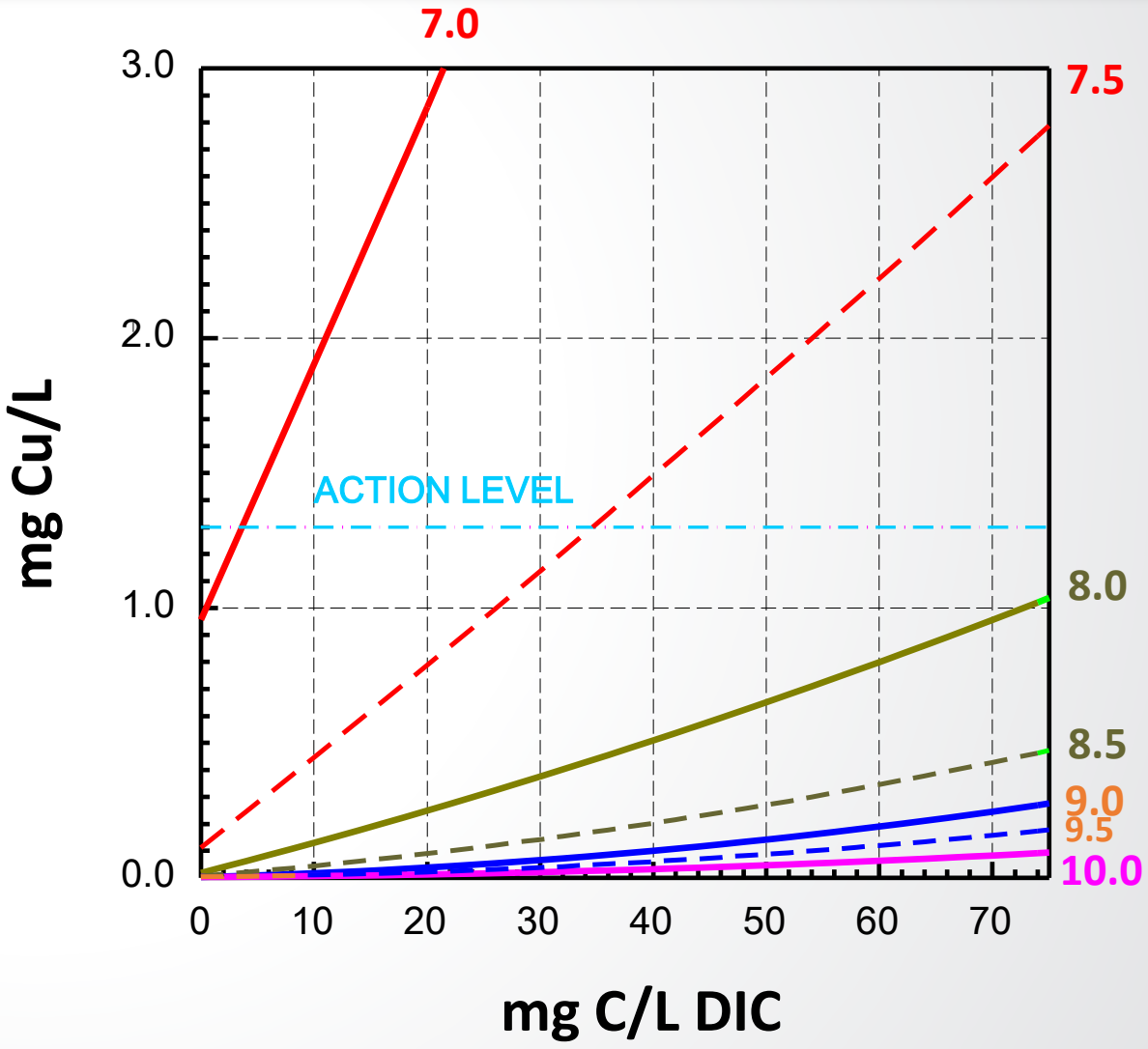
Effect of Dissolved Inorganic Carbonate and pH on Copper Solubility (23°C)



*Model predictions based on $Cu(OH)_2$

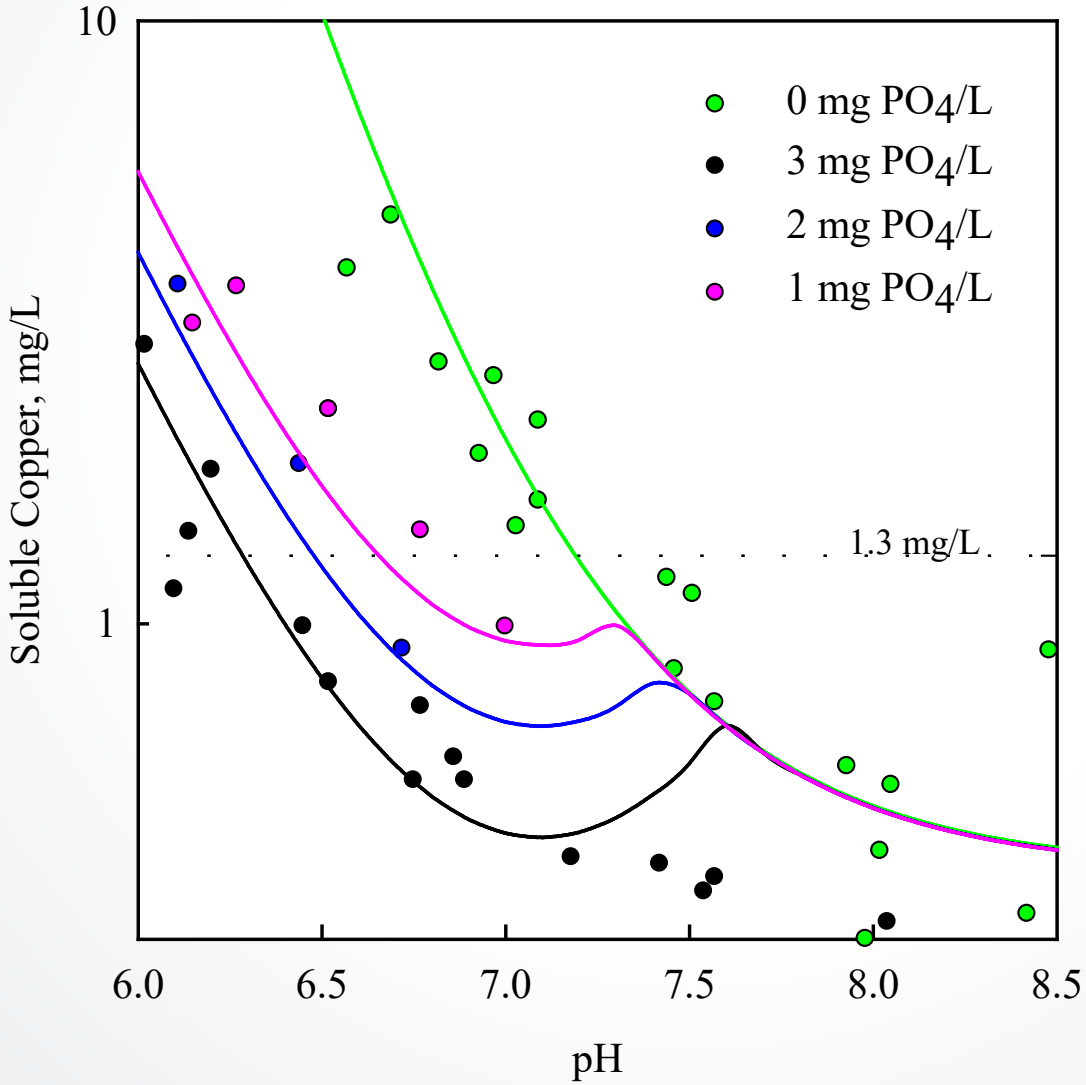
Cu(II) Solubility & pH Adjustment

- If **pH > 7.5**, no problems if **DIC < 35**
- If **DIC < 5**, no problems if **pH > 7**
- If **DIC > 35-40**, scaling & buffering prevents sufficient pH adjustment to solve problems



Batch Testing- *Solubility Results*

Effect of Orthophosphate and pH on Copper Solubility

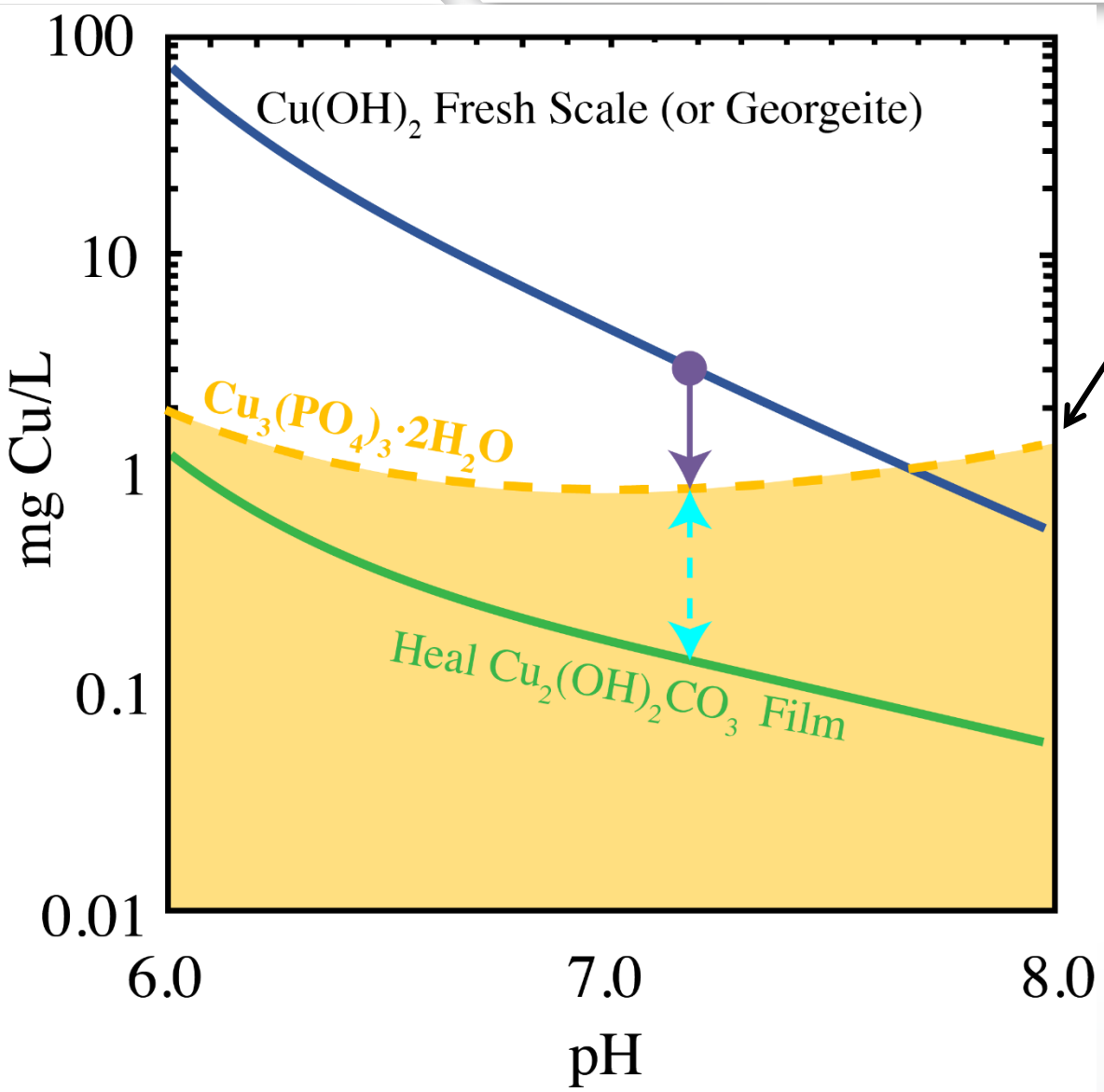


Water Quality Parameters:

- 23°C
- 10 mg C/L

Model predictions based on $Cu_3(PO_4)_2 \bullet 2H_2O$ and $Cu(OH)_2$

Orthophosphate Inhibits Aging



No real benefit at high pH

Aging Process is Impeded:

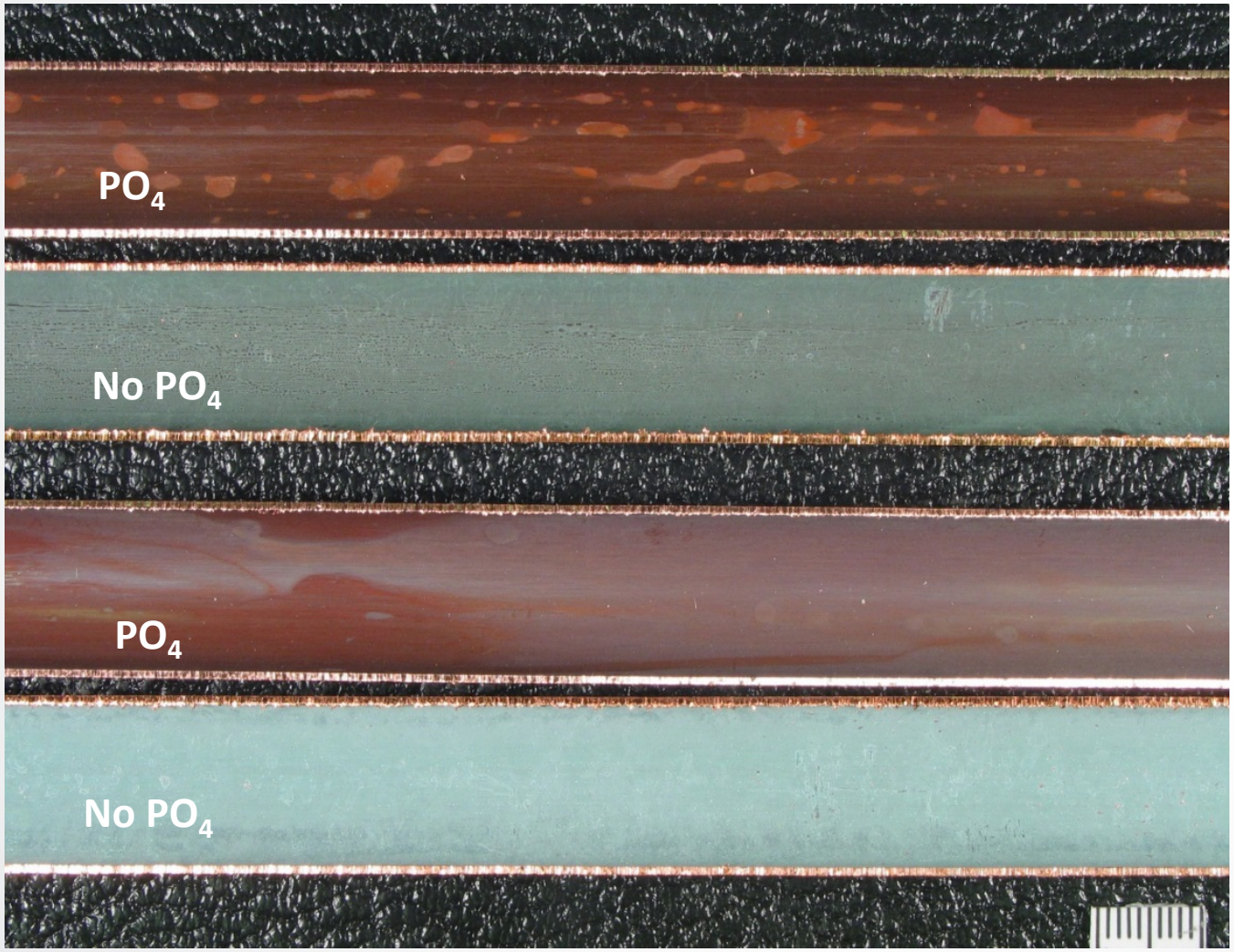
- Slows oxidation
- Prevents or drastically slows reaction with CO_3^{2-} or HCO_3^-
- Immediate benefit
- Does not continue on to stable malachite deposit

Orthophosphate Inhibits Aging

DIC = 50 mg C/L, PO_4= 3.0 mg/L (upper pipes)

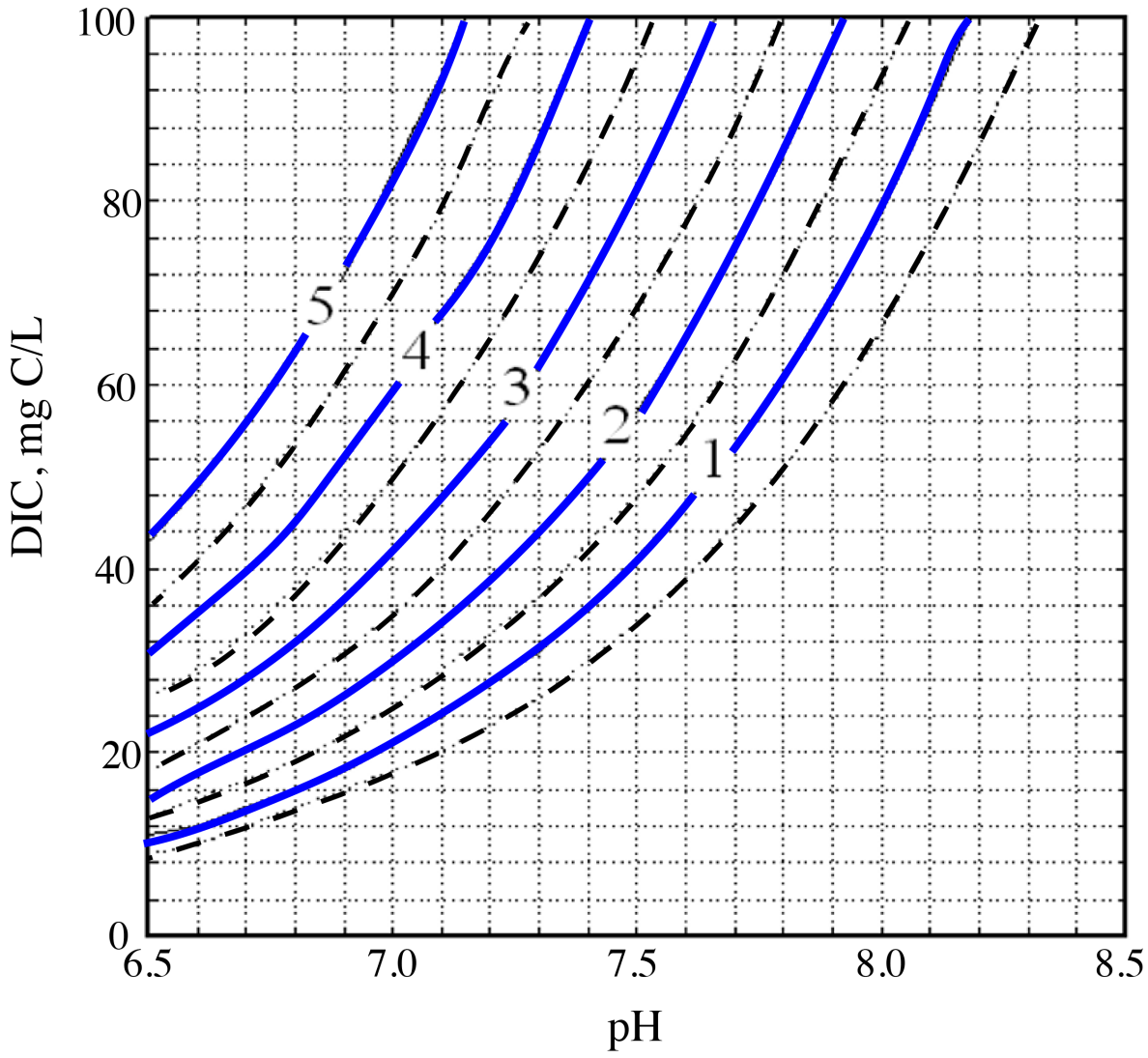
pH 8.0

pH 7.0



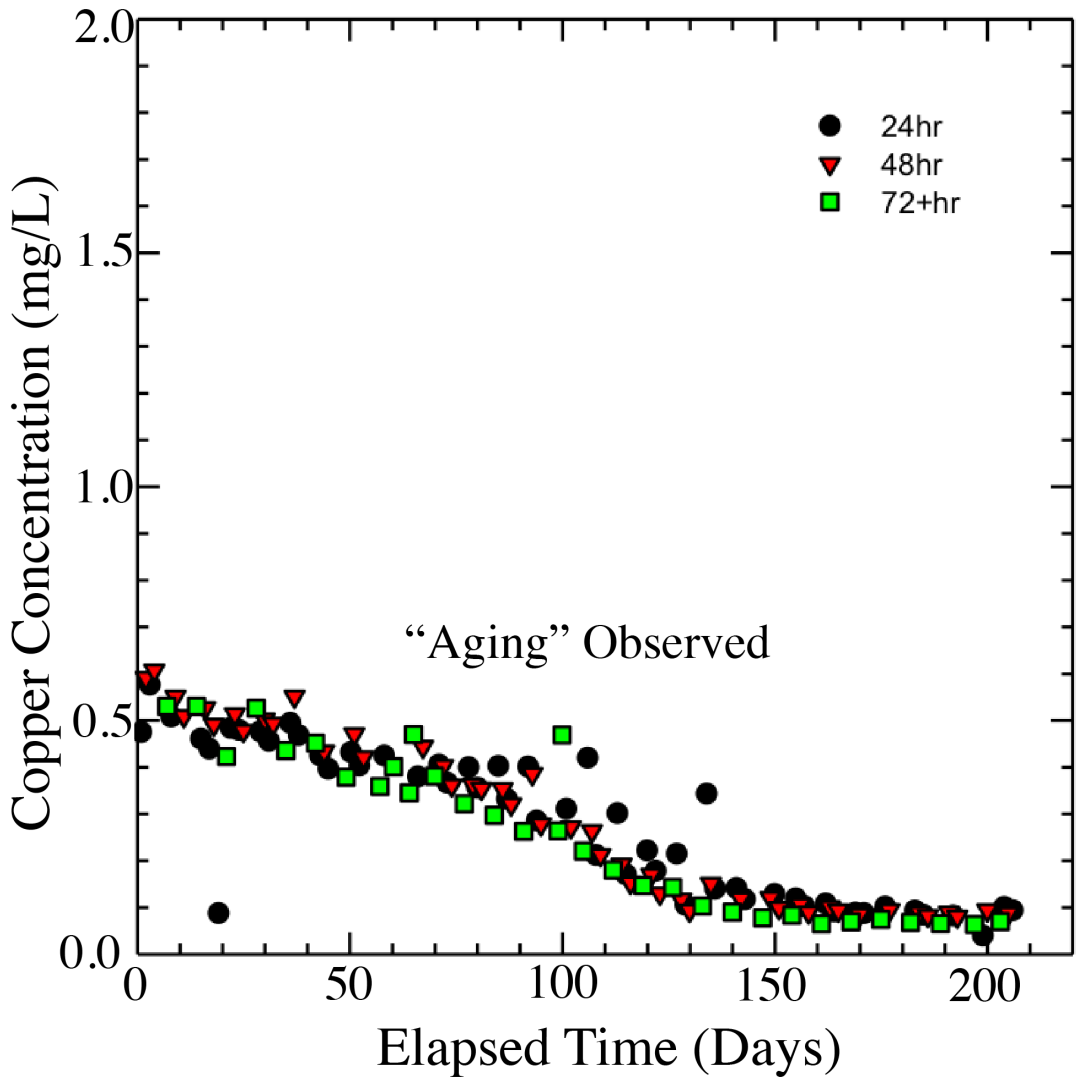
- Tradeoff between short-term health goal and long-term Cu passivation that takes years to decades.
- Aging won't proceed "normally" when orthophosphate is added.
- Enough ortho-P must be added to *immediately* offset elevation of copper by the carbonate level for new plumbing

Model-Predicted Orthophosphate Dose Necessary to Reach Copper Action Level (1.3 mg/L)



Copper Recirculation Test Loop

Copper Concentration over Time: Impact of Recirculation Time

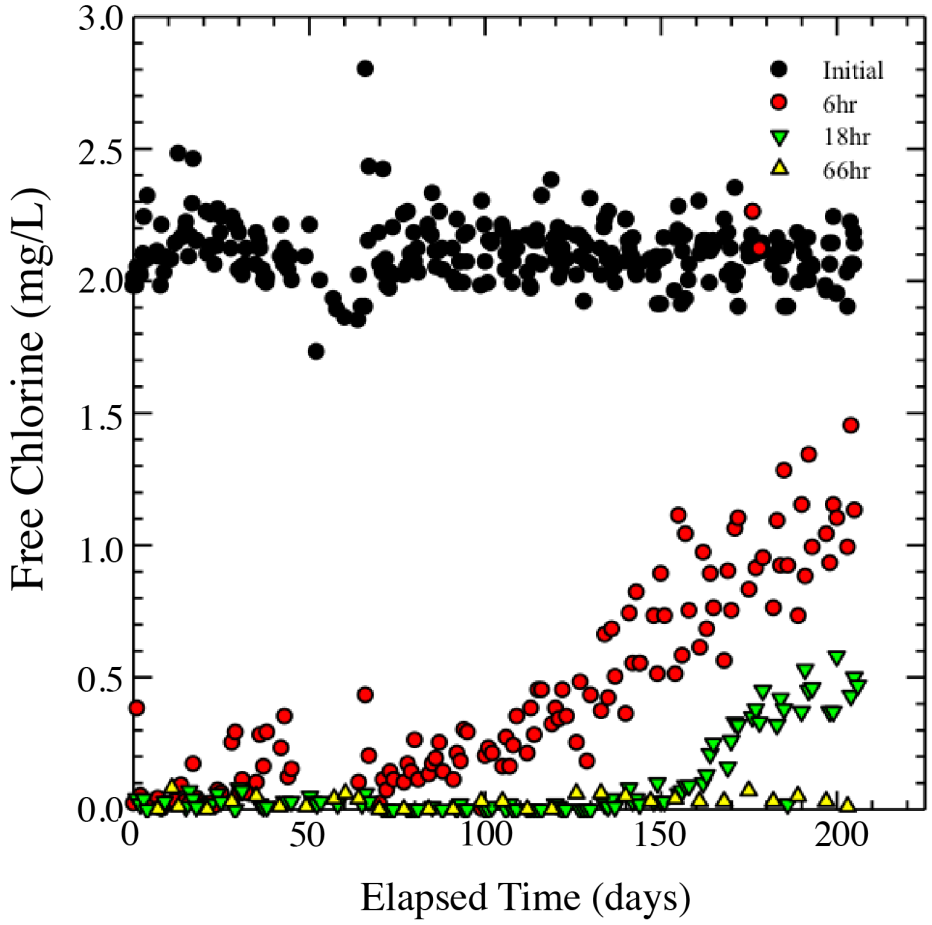


Water Chemistry Parameters:

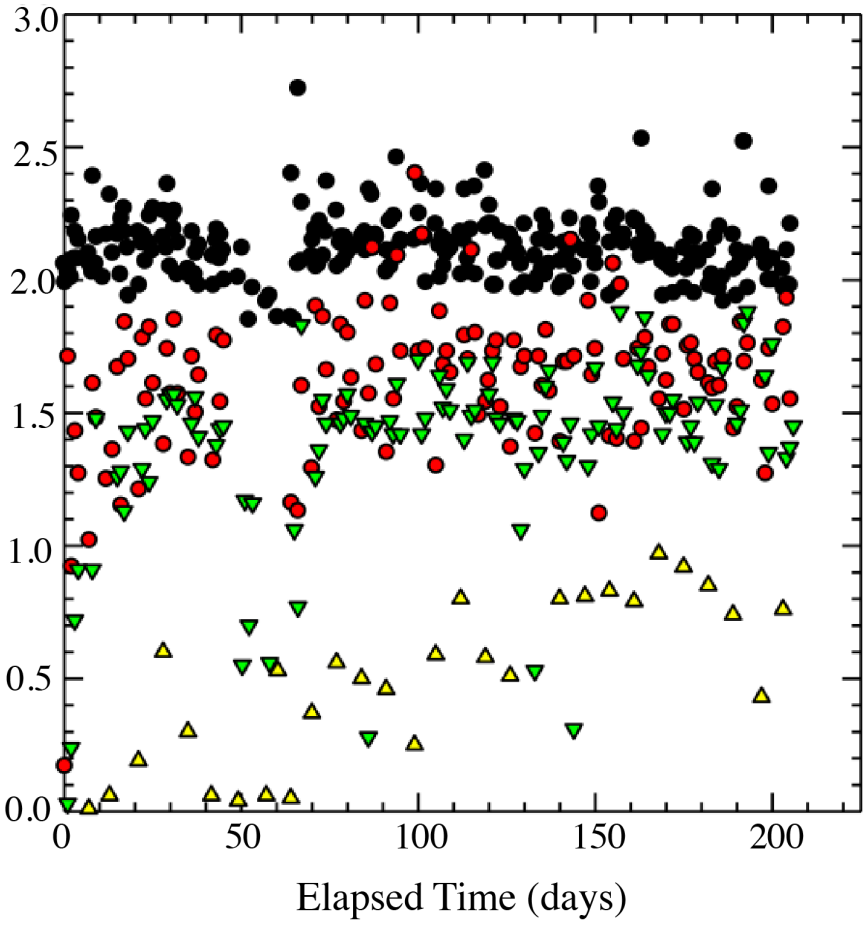
- pH 8.20
- 10 mg C/L
- 100 mg Cl^-/L
- 100 mg SO_4/L
- 2 mg Cl_2/L

Chlorine Demand Associated with Corroding Copper

Without PO_4



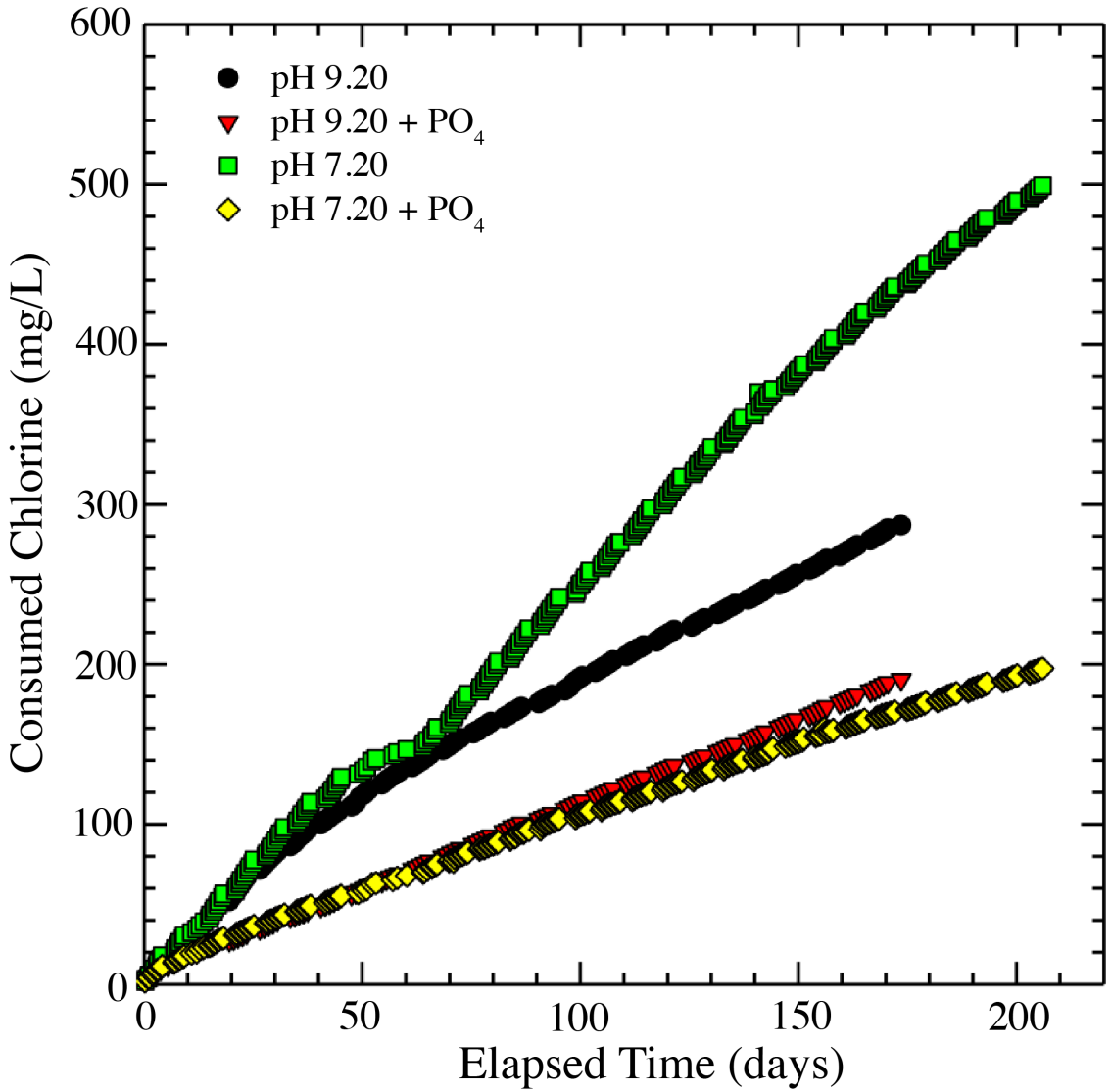
With 3 mg PO_4/L



Water Chemistry Parameters:

- pH 7, 10 mg C/L
- 100 mg Cl^-/L
- 100 mg SO_4^{2-}/L
- 2 mg Cl_2/L

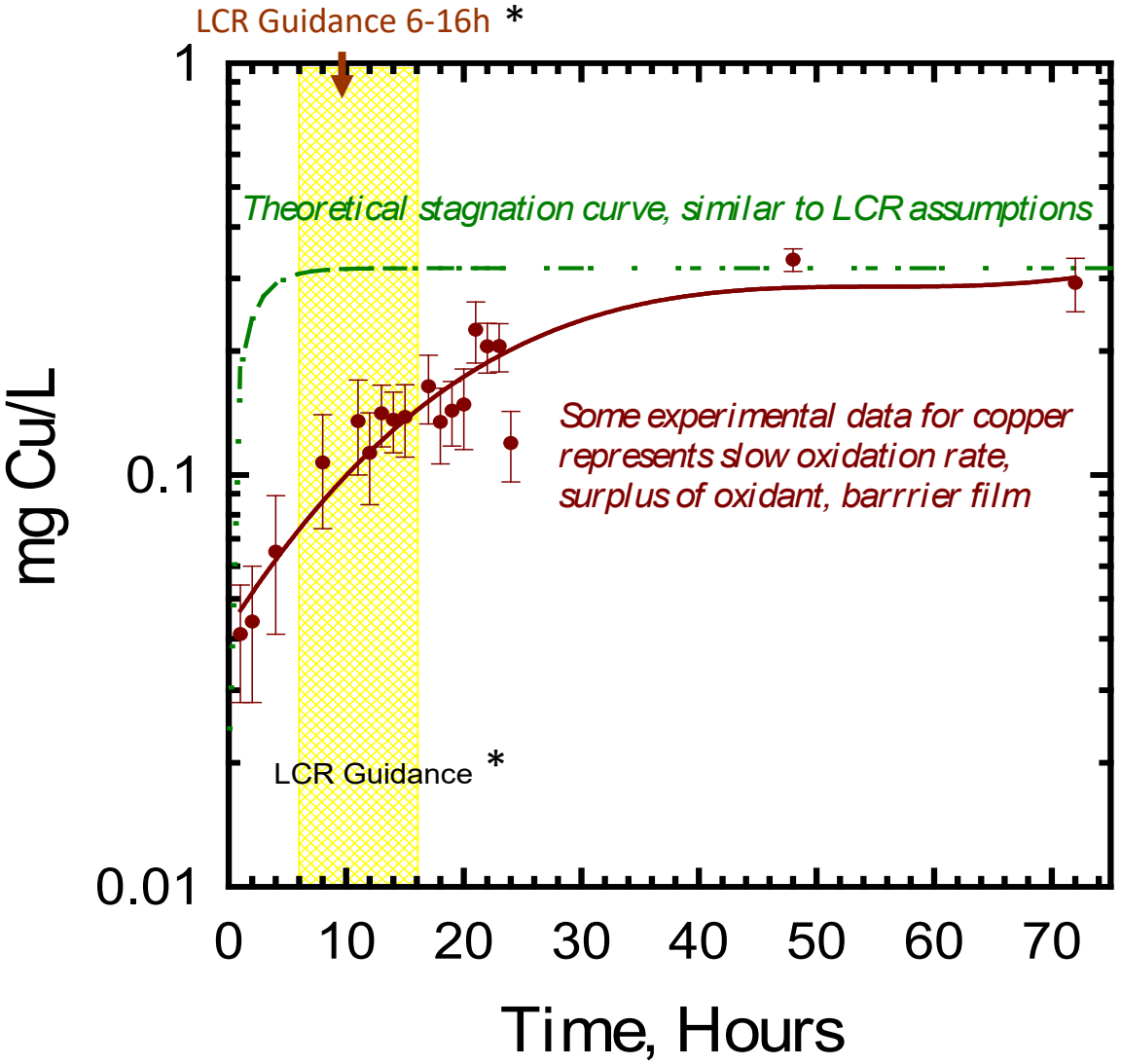
Total Chlorine Consumption over Time: Impact of Orthophosphate



Water Chemistry Parameters:

- 10 mg C/L
- 100 mg Cl^-/L
- 100 mg SO_4/L
- 2 mg Cl_2/L

Copper Stagnation Profiles with Time



- Green line: Theoretical stagnation curve, similar to LCR assumptions
- Some experimental data for copper represents slow oxidation rate, surplus of oxidant, barrier film

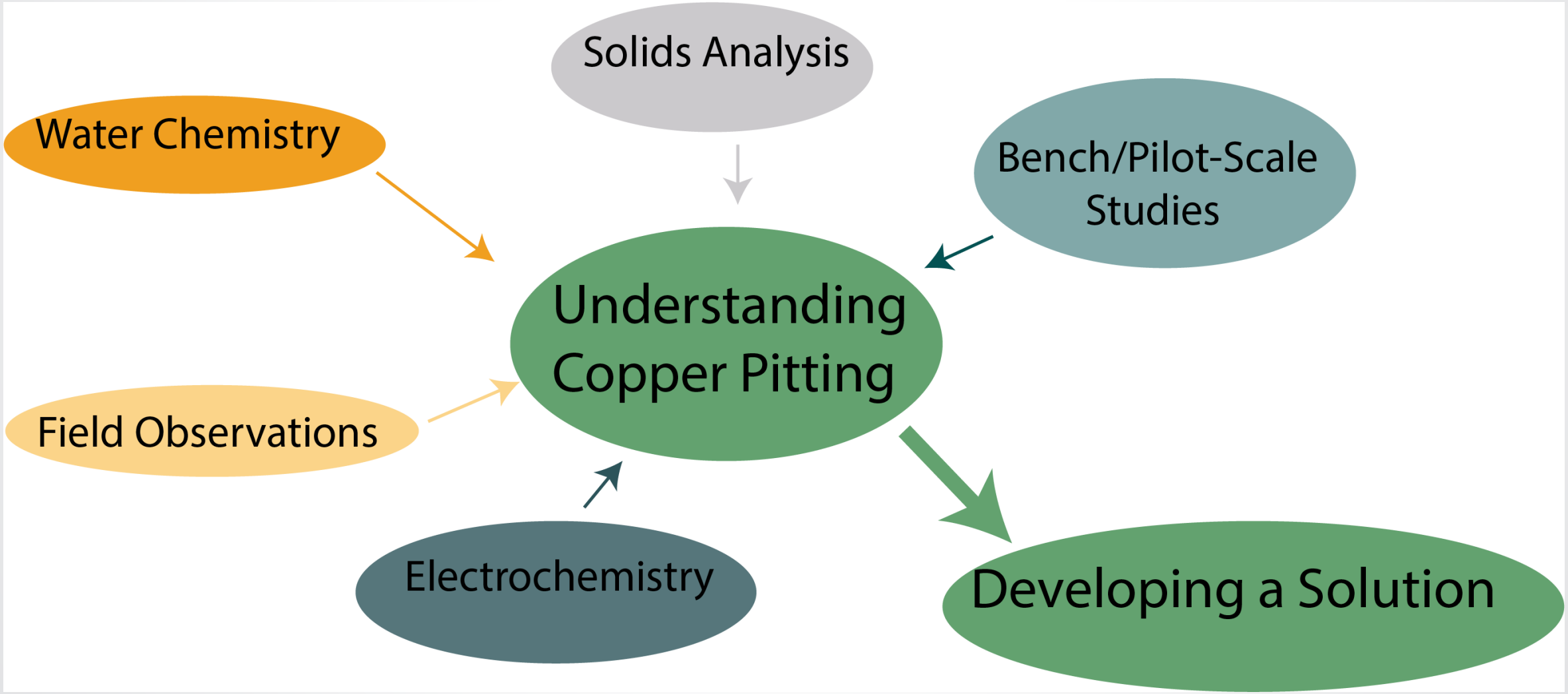
*This does not necessarily reflect the 2021 LCRR.

The Consequences of Copper Pitting

- Costly repairs
- Undetected leaks in walls and/or basements
- Pinhole leaks
  - Mold and mildew
  - Liability issues
- Complicated- many opinions, misinformation and passing of the blame

Note: Copper pitting typically does not cause high copper levels at the tap.

Tools for Understanding Copper Pitting and Developing a Solution

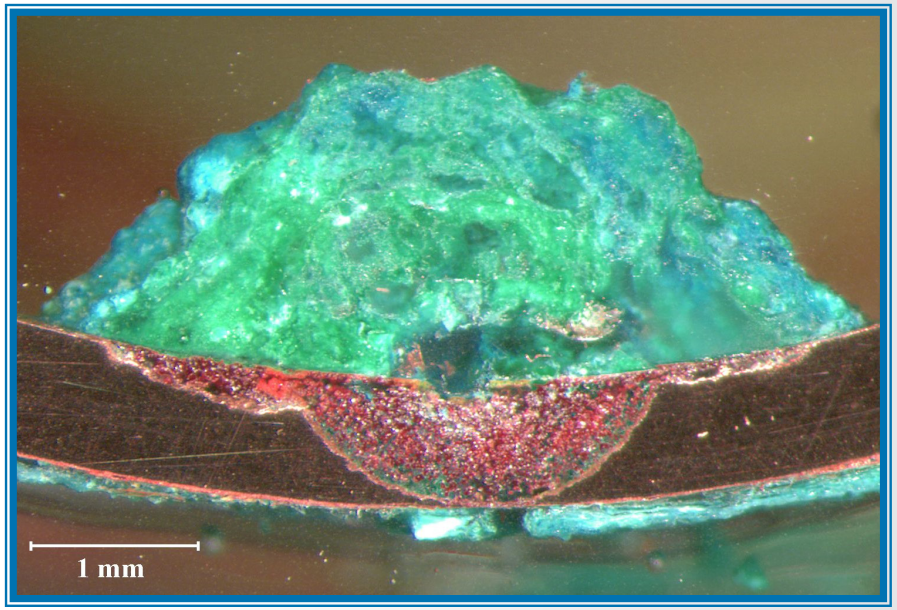


Reported “Causes” of Pitting Corrosion

- “Cheap” copper plumbing (imperfections)
- Poor plumbing workmanship
- Particles (aluminum, iron, others)
- Biofilm
- Disinfectant type
- Electrical grounding
- Others

Copper Pitting Corrosion and Water Quality

Based on technical assistance and practical experience and research finding, low alkalinity high pH water has been associated with copper pitting corrosion:



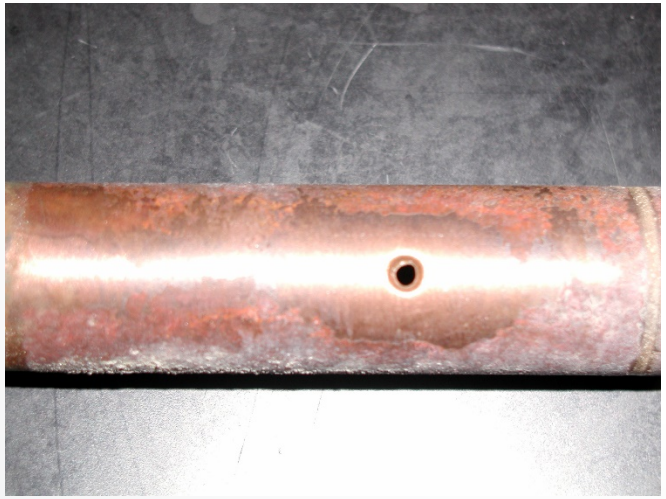
- Low DIC (< 10-15 mg C/L)
- High pH (> 8.5-9)
- Chloride (>10 mg/L)
- Sulfate (?)
- Hot and/or cold water

Other factors to consider include age of plumbing, history of treatment, corrosion control, and others.

Solids Analysis-Florida Study

dl000255 (outside)

dl000255 (inside)



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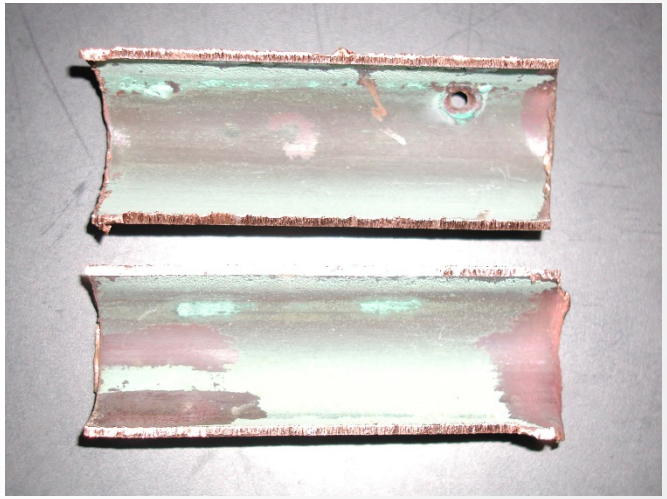

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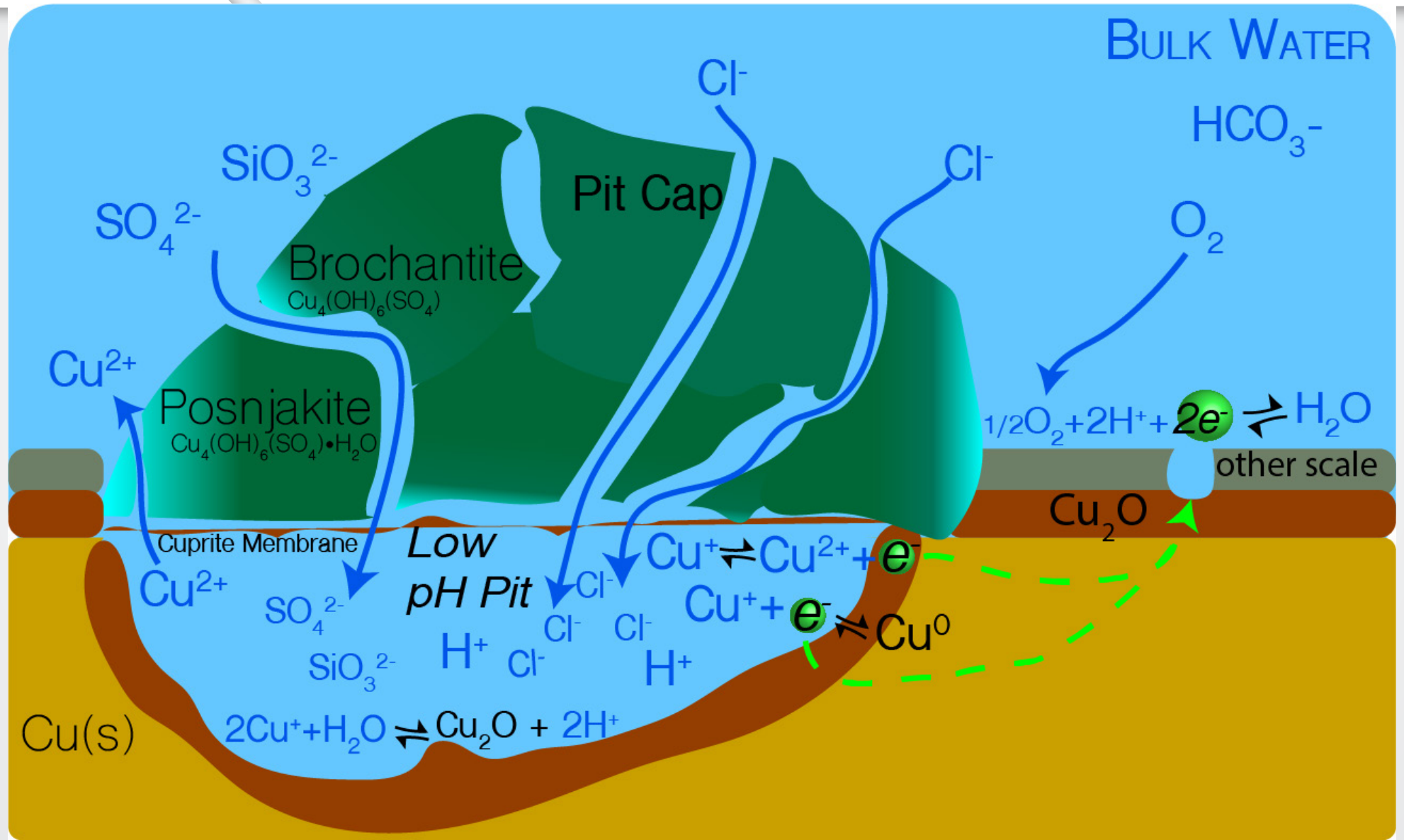
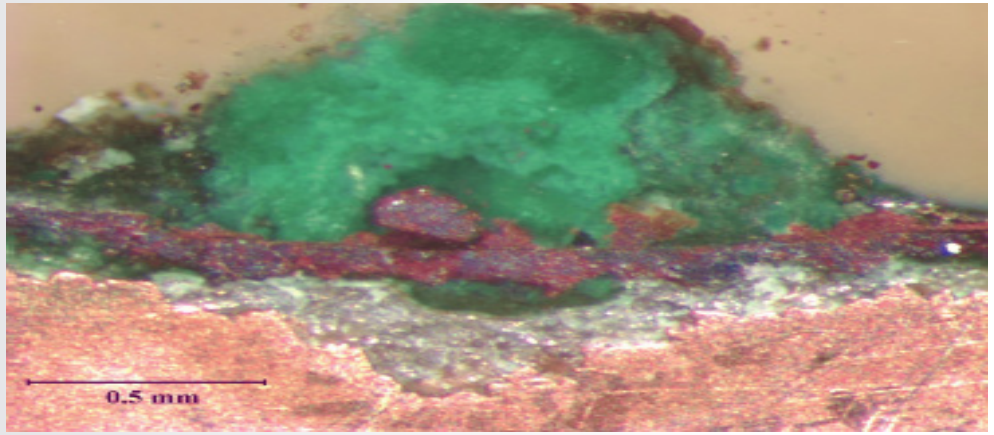
Conceptual Model of Copper Pit

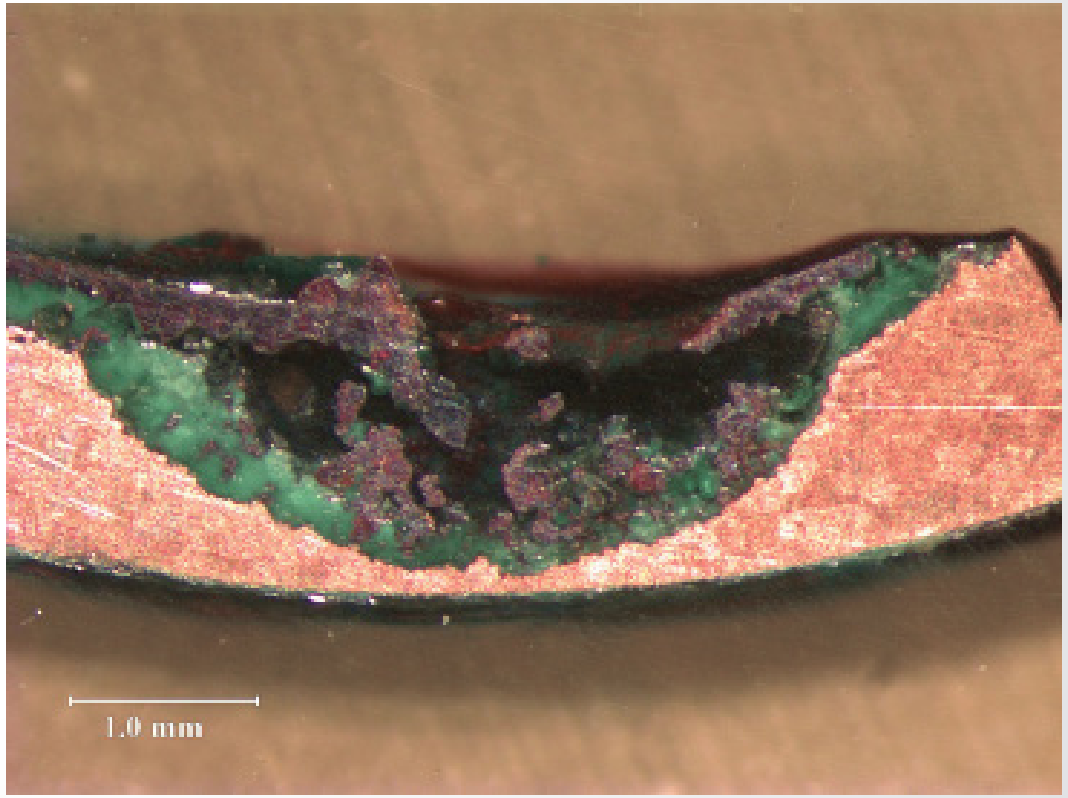


Solids Analysis-Florida Study

Pipe samples (DL00255)

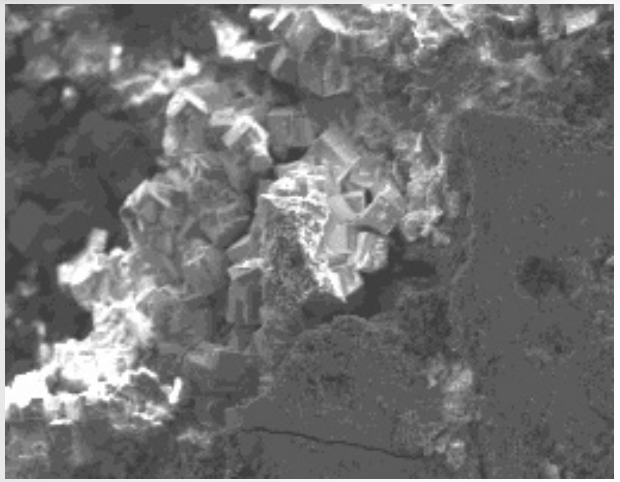
Stereo-microscope pictures of an epoxy mount of copper pitting and deposits





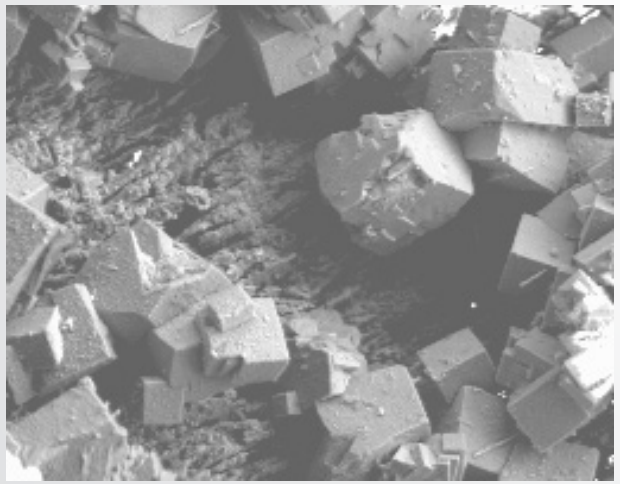
Solids Analysis- Florida Study

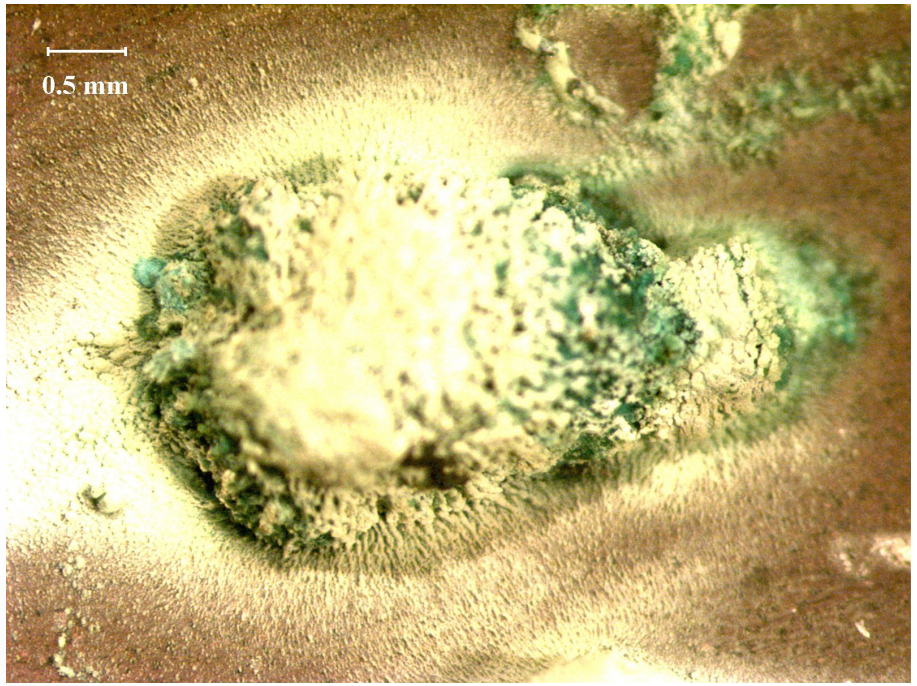
Features



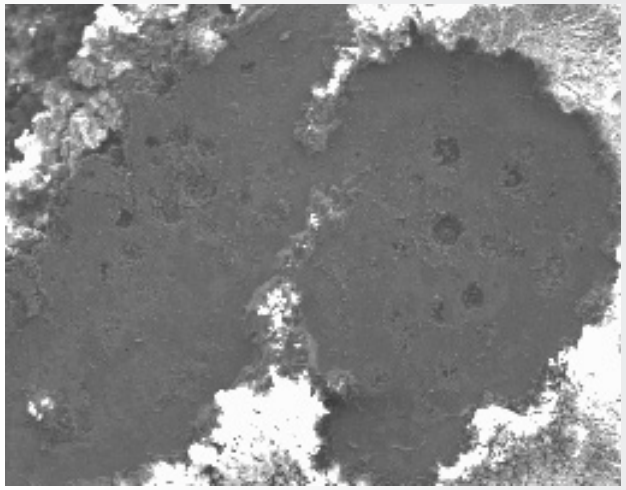
Pit membrane and contents

Pit contents



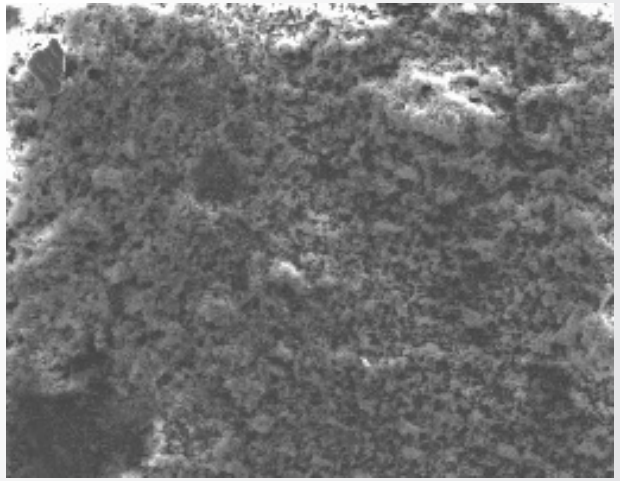


Pit cap and white deposits



Pit membrane

White deposits (Si, Al, Ca,O, S, others)



Site Characteristics

Water chemistry

Sample	Ca, mg/L	Cl, mg/L	Mg, mg/L	SiO_2, mg/L	SO_4, mg/L	Free Cl_2/L	Total Cl_2/L	TALK, mg/L $CaCO_3$	TIC, mg C/L	pH
Butler County, cold	27	64	27	10	120	0.2	0.3	39	8.8	8.80
Butler County, hot	28	65	28	10	125	0.4	0.5	38	8.1	8.30
Florida test site Florida Test Site	43	47	20	14	168	1.0	4.3	46	11.0	8.04
Site 1, Ohio*	26	45	24	10	77	na	na	77	15.9	9.09
Site 2, Ohio*	39	73	10	6.3	70.6	0.47	na	53	13	8.22

- Site 1 and 2 in Ohio use water from same aquifer as Butler County, Ohio and treat their by lime softening with the exception being that they both add sodium hexametaphosphate (0.75 to 1 mg PO_4/L) for corrosion control or prevention of filter clogging.

Neither has experienced copper pitting problems in the DS.

Pilot Scale Research

Copper Recirculation ("Recirc") Study

- EPA research was conducted to study copper release (uniform corrosion) in the early 1990's
  - Mike Schock (US EPA)
- Foundation for current thinking on copper levels at the consumer's tap
- Experimental conditions produced localized corrosion attributed to water chemistry
- Synthetic waters used in most experiments: water quality closely controlled

Pilot Study- Copper Recirc Study

Water chemistry from lab experiments

pH	SO_4 (mg/L)	pH	Temp	Ca	Cl	Cl_2	SO_4	TIC
7	0	7.02	22.6	4.7	61	0.63	3.9	10.4
	5	7.00	22.8	4.3	66	0.65	6.8	9.9
	50	6.99	22.9	4.4	63	0.63	49.2	10.2
	150	7.00	22.8	4.4	66	0.59	150.2	9.8
8	0	7.98	23.0	3.8	56	0.56	0.2	10.5
	5	7.99	23.2	5.0	60	0.59	3.8	10.4
	50	7.99	23.1	4.9	53	0.62	50.2	10.1
	150	7.98	23.0	4.9	53	0.72	148.2	10.4
9	0	8.98	22.9	5.3	28	0.65	0.1	10.8
	5	8.97	23.1	4.9	28	0.66	4.7	10.5
	50	8.98	23.0	4.9	26	0.78	47.7	10.3
	150	8.98	22.8	5.0	23	0.81	143.5	10.3

* All units are in mg/L, TIC is in mg C/L units

Water Quality Parameters:

Florida water: pH= , SO_4= 121 mg/L, Cl=47 mg/L, TIC= 9.8 mg C/L

Butler Co. water: pH= 8.9, SO_4= 120 mg/L, Cl=64 mg/L, TIC= 9.8 mg C/L

Pilot Study- Copper Recirc Study

Pipe cross-section at pH 9

0 mg $[SO_4]$/L

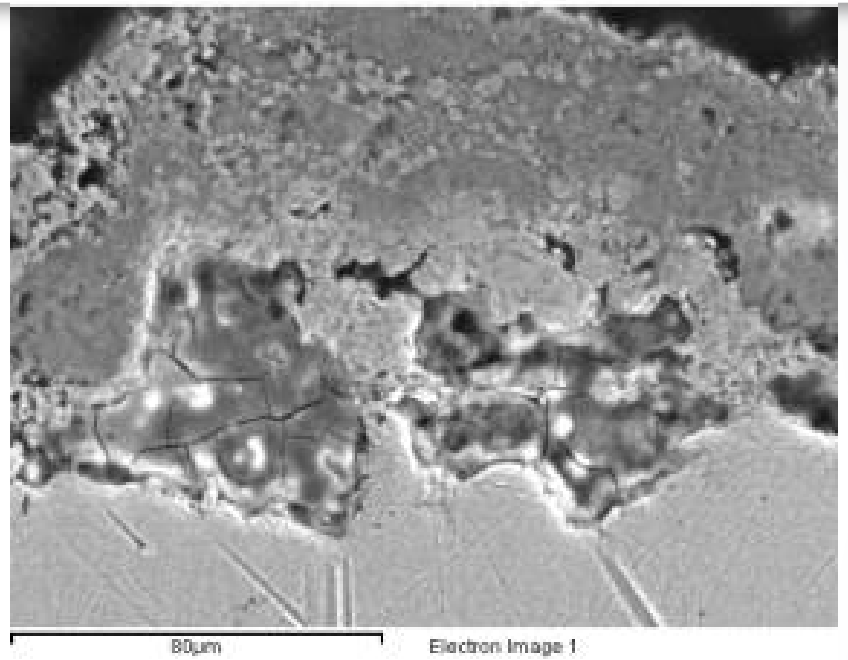
5 mg $[SO_4]$/L

50 mg $[SO_4]$/L

150 mg $[SO_4]$/L

Pilot Study- Copper Recirc Study

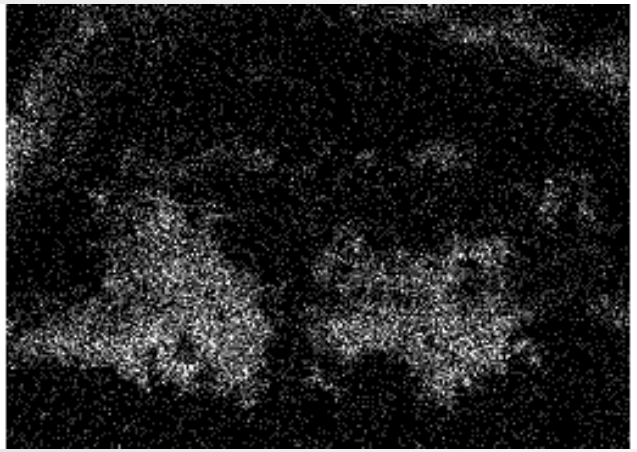
SEM-EDS Evidence for Localized Corrosion



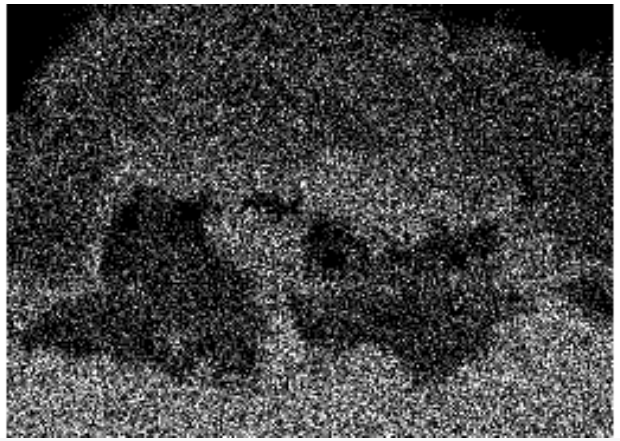
Water Quality Parameters:

- pH 9
- 5 mg SO_4/L
- 28 mg Cl/L

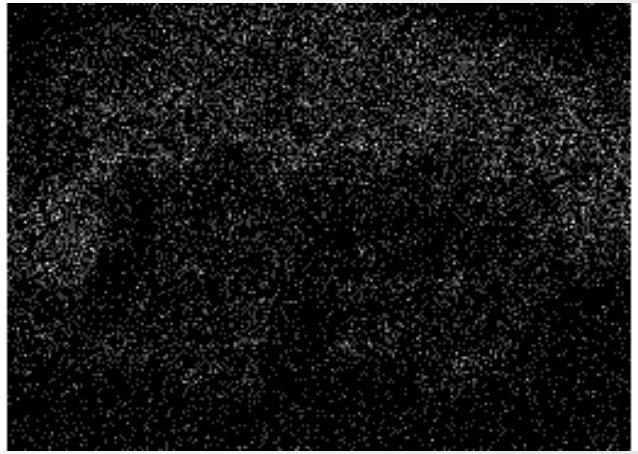
Chlorine



Copper



Oxygen



Pilot Study- Copper Recirc Study

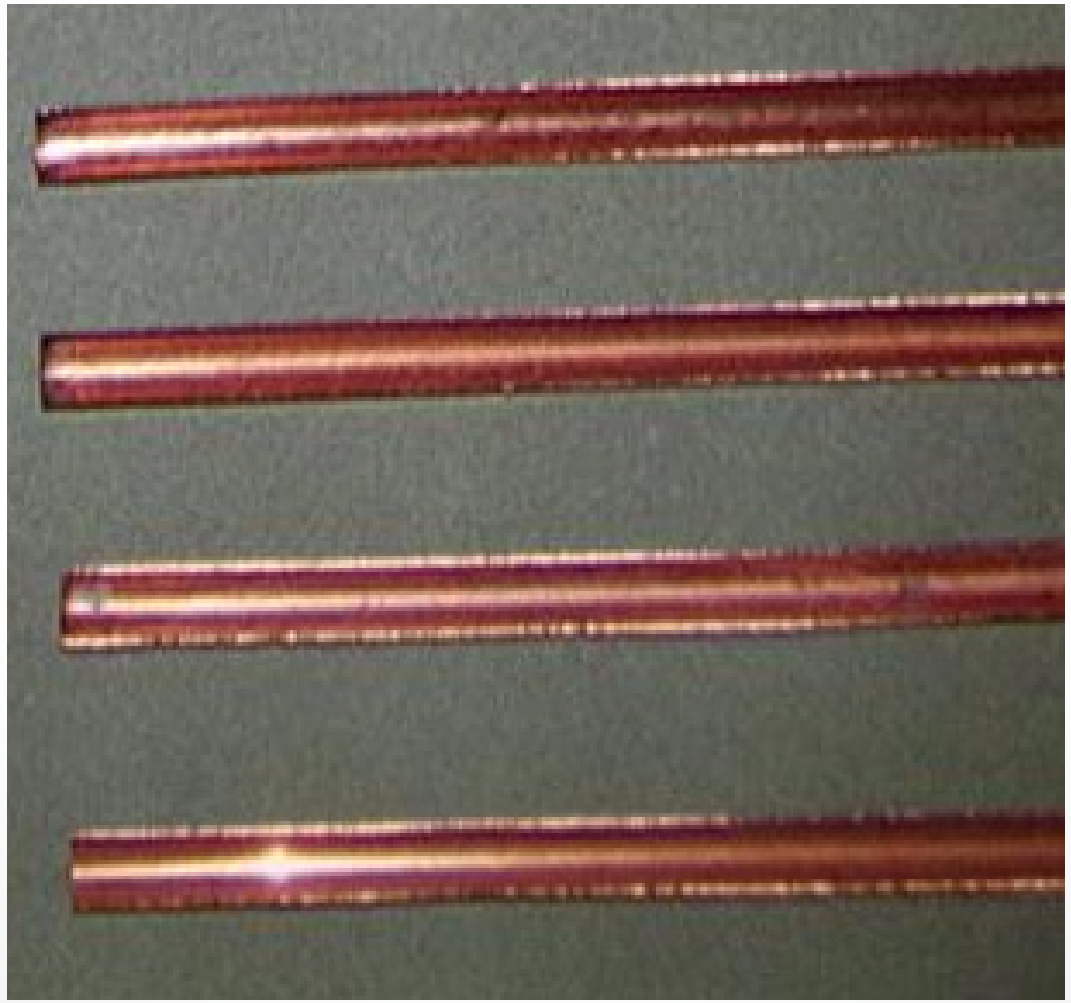
pH

6.5

7.0

8.0

9.0



Water Quality Parameters:

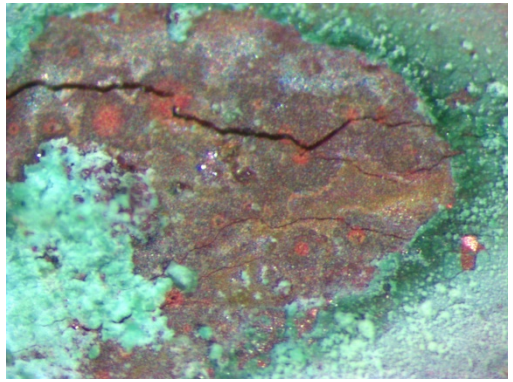
- 3 mg PO_4/L
- DIC=5 mg C/L

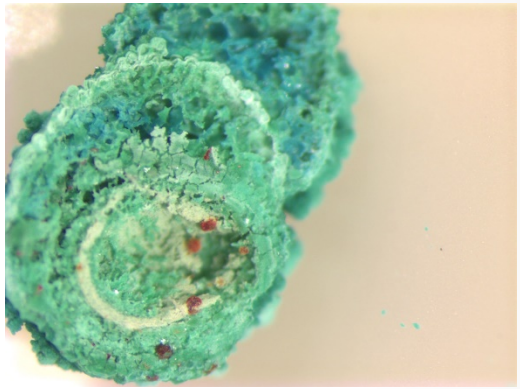
Tracking Pitting Corrosion and Pinhole Leaks

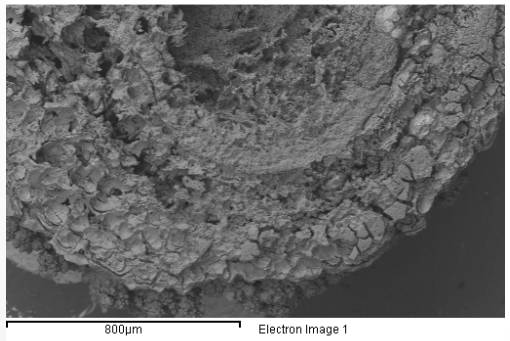
- DS water quality analysis
- Leak detection company results
- County building permit records
  - Already leaking
  - Preventative
- Simple copper pipe loops
- **Pipe surface analysis**

Phosphate added after Pitting Corrosion is Well Established

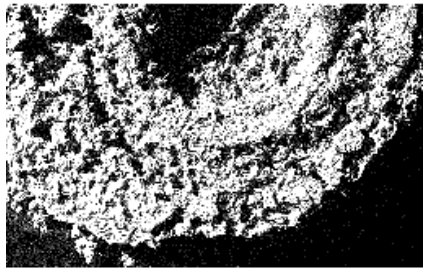
Pit Cap Analysis 10 months after blended phosphate addition



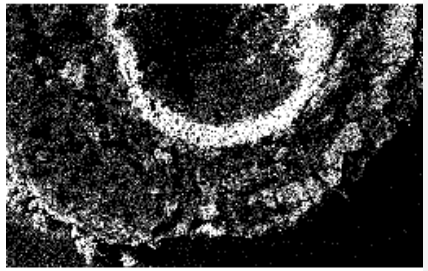




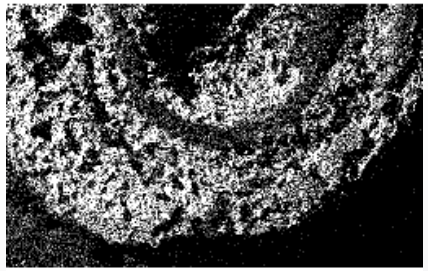
Elemental Mapping



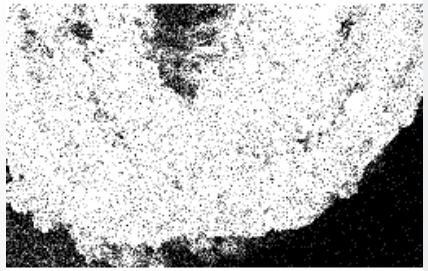
O Ka1



P Ka1



S Ka1



Cu Ka1

Conclusions: Water Quality Matters

- Copper minerals on pipe surfaces age from a relatively soluble to relatively insoluble ones. Worst case copper sites will be associated with newer plumbing.
- Copper(II) solubility is greatly sensitive to DIC and pH.
- Orthophosphate reduces copper solubility (including high DIC waters) but interferes with the aging process
- Copper pitting corrosion is very complicated and associated investigations must consider multiple factors.
- Although not the only condition where copper pitting cases are observed, low DIC, high pH water with significant amounts of chloride are likely to be problematic.
- Phosphates may help prevent pitting and possibly slowdown active pits.

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Thank you

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