Water Research Foundation
Celebrating 50 Years 1966–2016

CCT and WQPs What's New

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EE&T,INC
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advancing the science of water

Historical Perspective on Managing Corrosivity

- Longevity of piping, appurtenances, and plumbing
- Reliable delivery of water
- Preventing staining/red water
- Control of release of metals (Particularly iron)

We still have to achieve iron corrosion control

Historical Corrosion Management—Still Important

- Iron corrosion
  - Prevent Tuberculation
  - Prevent pipe loss
  - Prevent red water

- Controlled by
  - Ferric oxides & calcium carbonate films at pH >8
  - Polyphosphate addition –NOT orthophosphate

Iron corrosion control is not necessarily lead corrosion control

Improve Corrosion Control Treatment

(Section 3.3.1, pp 29-30)

- LCRWG recommends:
  - EPA release a revised CCT guidance manual and update regularly to reflect new science
  - EPA provide increased assistance to PWSs and primacy agencies
  - PWS review of updates to guidance to determine if CCT is based on best science
  - CCT reassessment when PWS changes treatment or source
  - Better use of water quality parameters (WQPs) for process control
  - More rigorous data review, control charts, process controls
  - PWSs not practicing CCT demonstrate water quality characteristics remain in place

Presented to NDWAC by EPA Summarizing WG Report

Assessing the Effectiveness of CCT

(Section 3.4.2, pp 33)

- Tap samples would be reported to primacy agency on a routine bases, and include information on sampling protocols used
- The PWS should maintain the data for review to identify trends and changes; data would be available for public review
- Data to be reviewed during sanitary surveys
- Annually, at the request of the primacy agency, the PWS would provide a report which includes the three most current years of data
- If the 90th percentile of the three years of data exceeds the "System Action Level" then the PWS must assess the cause and potentially re-evaluate CCT or take other actions prescribed by the primacy agency
- Source water and treatment changes would necessitate a review of the tap sampling data in consultation with the primacy agency

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WQP Monitoring Requirements

(Section 3.4.1, p 31)

- Tailor WQPs based on the individual PWS's CCT plan, increase the frequency of WQP monitoring for process control, and ensure sites are representative of the distribution system (DS)
- EPA should review and consider adding to the list of WQPs in the LCR based on new science
  - The new information would be disseminated through EPA's CCT guidance manual
- WQP data should support a more rigorous review process such as control charting and other techniques to fine tune operations, reduce variability in DS and detect excursions

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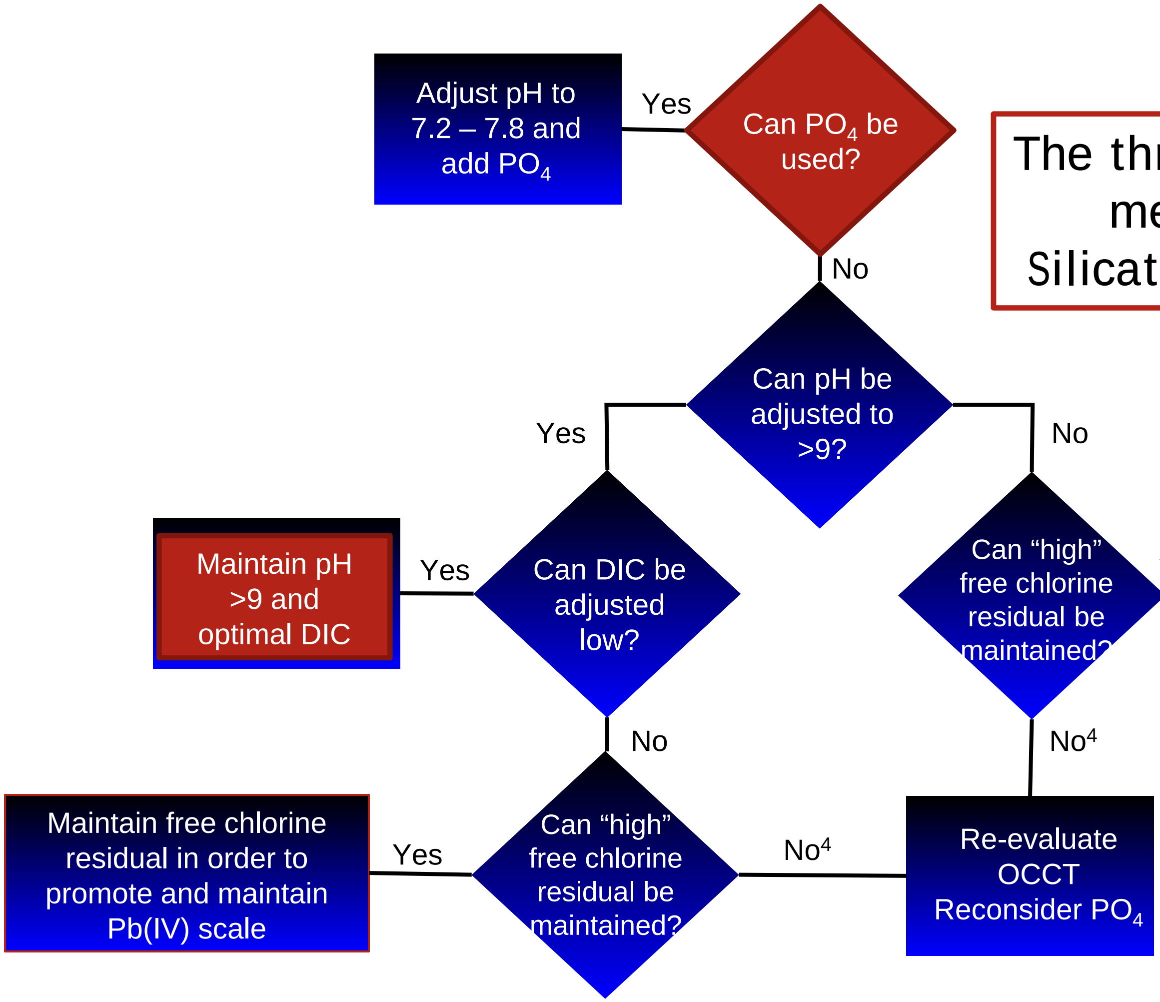
Lead Corrosion Control Strategies

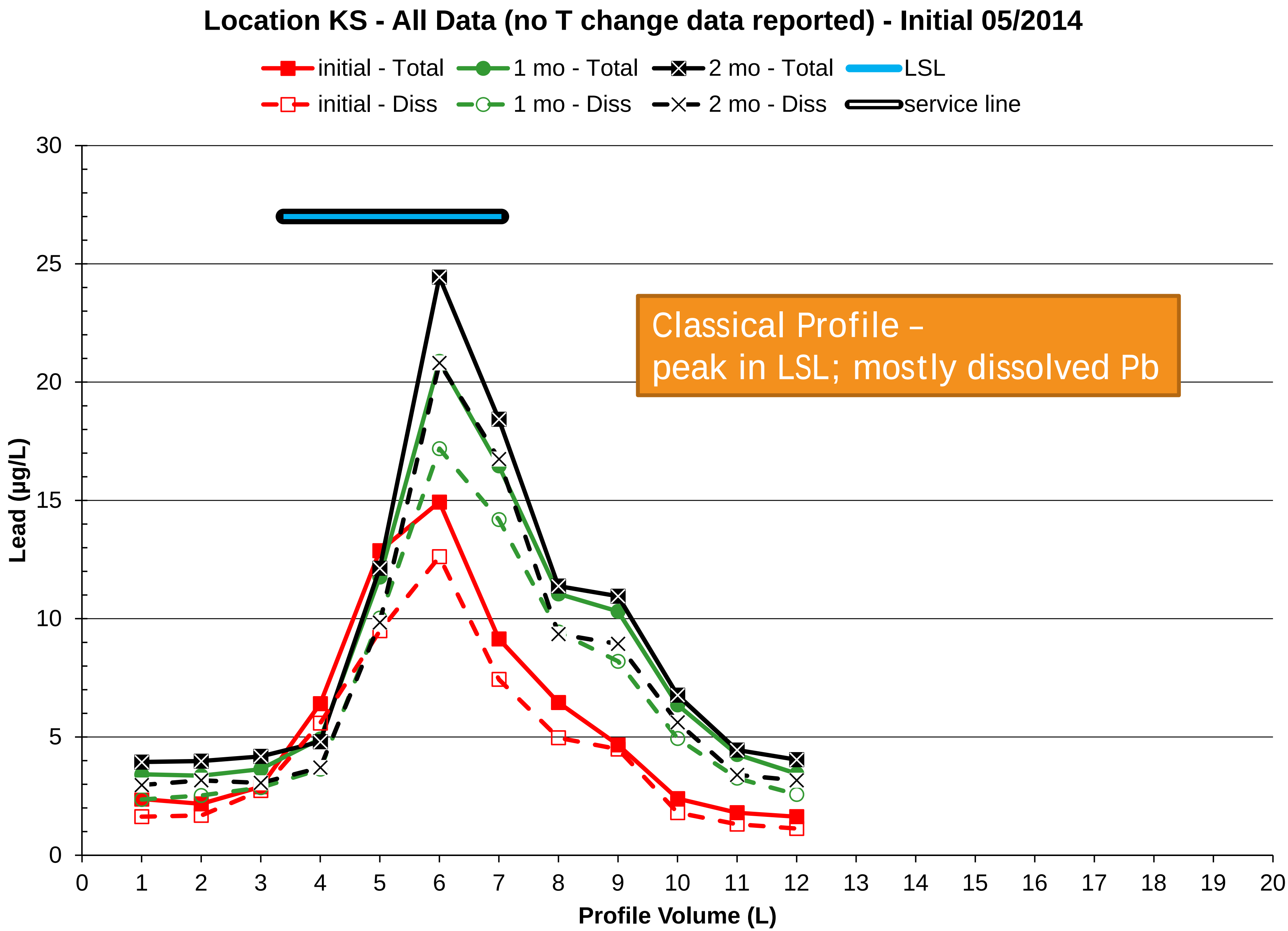


The three primary lead CCT methods.
Silicates can also be considered

Source: Brown, R. A., N. E. McTigue, and D. A. Cornwell. 2013. Strategies for assessing optimized corrosion control treatment of lead and copper. *Journal AWWA* 105(5) May 2013: 62 – 75. **permission pending*

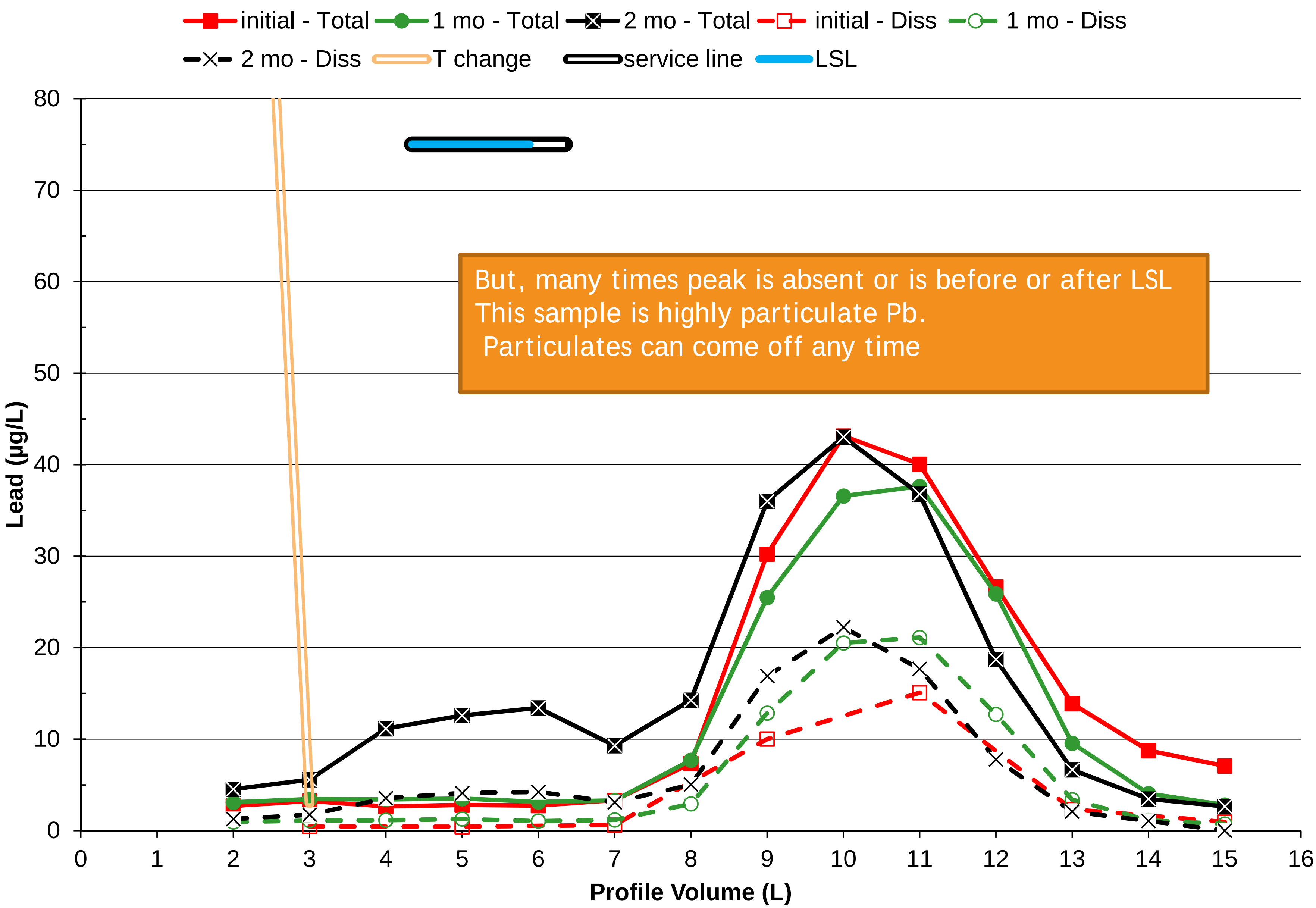
What Have We Learned about Pb CCT

- Particulate lead is very important and harder to control and harder to predict release
- There are often higher lead levels at the tap than 1st draw
- Houses are unique
- Polyphosphate is not a lead corrosion inhibitor—might make Pb worse
- Changes in ORP can cause lead releases



Location KS - All Data (no T change data reported) - Initial 05/2014
initial - Total
1 mo - Total
2 mo - Total
LSL
initial - Diss
1 mo - Diss
2 mo - Diss
service line
Classical Profile –
peak in LSL; mostly dissolved Pb
Lead (µg/L)
Profile Volume (L)
0
5
10
15
20
25
30
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

Location QA - All Data (initial T change missing) - Initial 11/2011



But, many times peak is absent or is before or after LSL
This sample is highly particulate Pb.
Particulates can come off any time

AN EVALUATION OF UTILITIES CONDUCTING VARIOUS LEAD SAMPLING PROTOCOLS

Lessons Learned about Lead Particles

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WRF & AWWA WITAF

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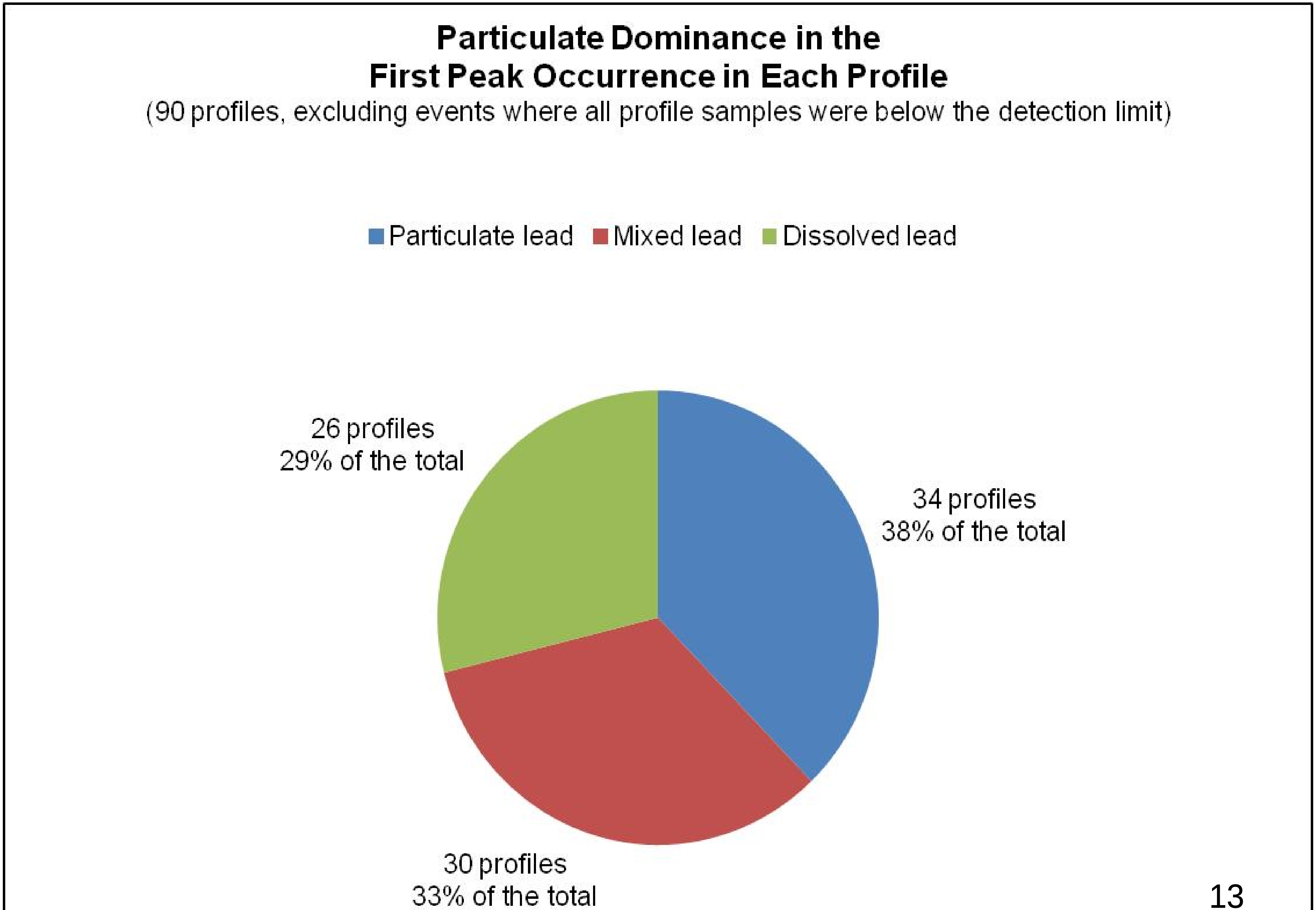
Participating Water Systems

- 8 participating water systems
- 3 use free chlorine, 5 use chloramines
- All well below AL
- 6 systems use orthophosphate
  - pH 7.2 to 7.6, except one >8.0
  - Target PO_4 residual = 0.3 to 0.8 mg/L as P
- Other systems
  - One system = pH/alkalinity adjustment (pH ~9.3)
  - One system uses pH/alkalinity (pH ~8.5) plus Pb(IV)
- Sample Collection and analysis
  - 37 locations (houses)
  - 96 profiles


Particulate Dominance in the
First Peak Occurrence in Each Profile
(90 profiles, excluding events where all profile samples were below the detection limit)
Particulate lead
Mixed lead
Dissolved lead
26 profiles
29% of the total
34 profiles
38% of the total
30 profiles
33% of the total

Particulate Pb in all Profiles

- Total Profile Samples 1,152 (96 times 12)
- Of these
  - 33 % dissolved lead
  - 67 % had particulate lead
  - 31 % primarily particulate lead
- 143 of these 1,152 samples were ≥15 µg/L - of these
  - 31 % dissolved lead
  - 69 % had particulate lead
  - 21 % primarily particulate lead
- Overall, as with peak, only about one-third of all samples were dissolved lead

Additional Particulate Findings

- Independent of corrosion control approach, no participating utility was dominated system-wide by any lead form
  - i.e., none were all "particulate dominated" and none were all "dissolved dominated"
- Individual houses
  - 12 % of houses were always "dissolved dominated"
  - 21 % of houses were always "particulate dominated"
  - 67 % were dominated by particulate Pb some dates, and dissolved Pb other dates

❖ **Particulate lead release is a major factor in lead levels**

❖ **Why do we get particulate lead?**

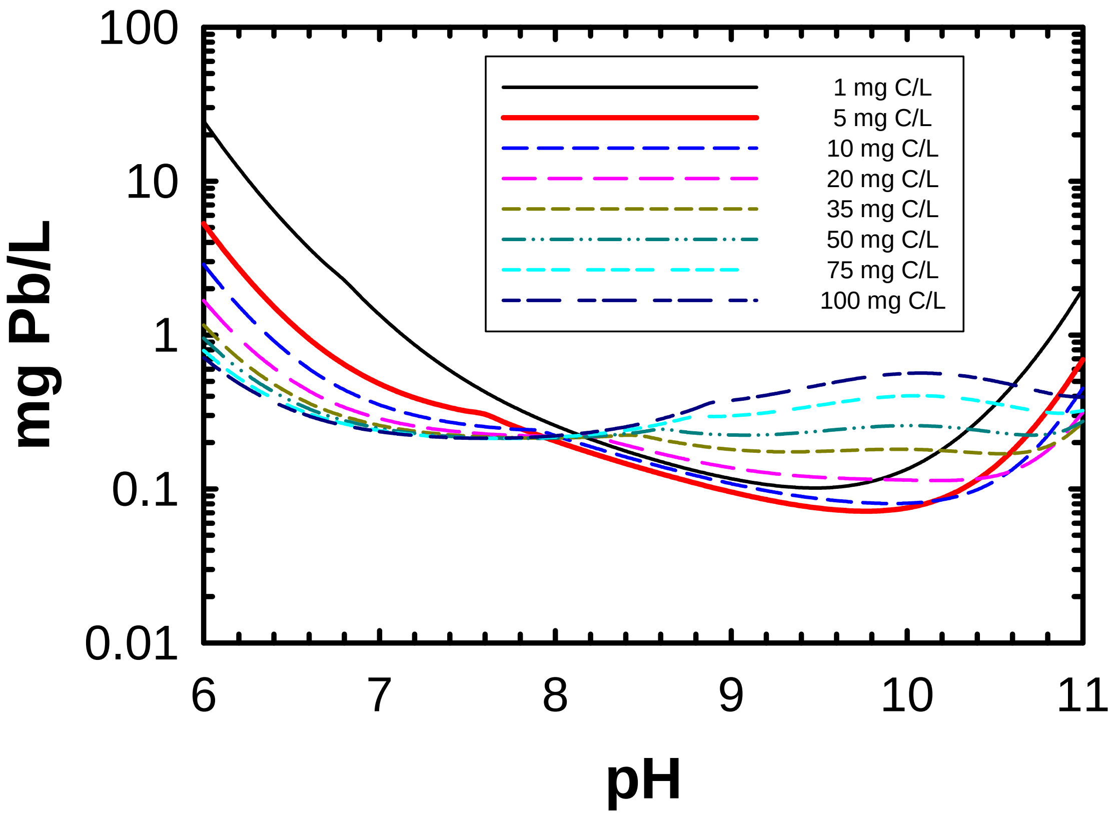
Factors Governing Pb Levels

- Sampling protocol
- Intrinsic Pb solubility of surface material (water chemistry)
- Rate of dissolution in short stagnation times
  - Galvanic driving force
  - Diffusion from surface (reaches steady state)
- Length of contact with lead source
- Nature of lead release
  - Particulate
  - Soluble

Source: Michael Schock EPA presentation to NDWAC working group

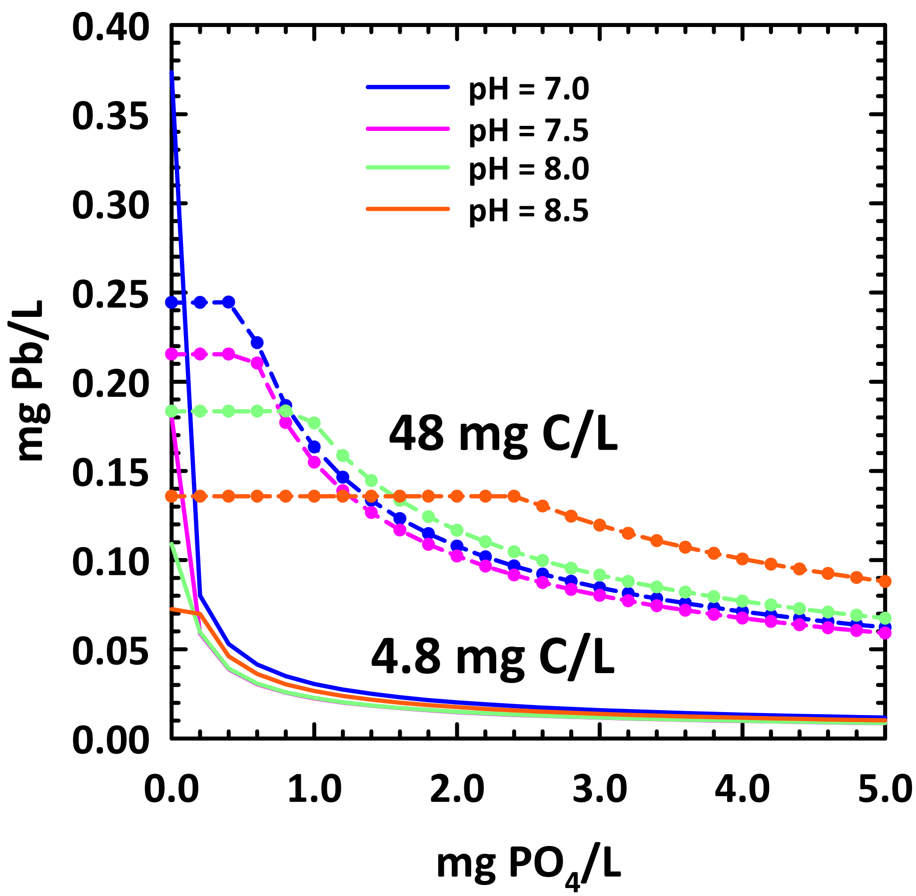
Lets First Look at Lead Solubility—Dissolved Lead

Classic Pb(II) Solubility, fresh surface



Source: Michael Schock EPA presentation to NDWAC working group

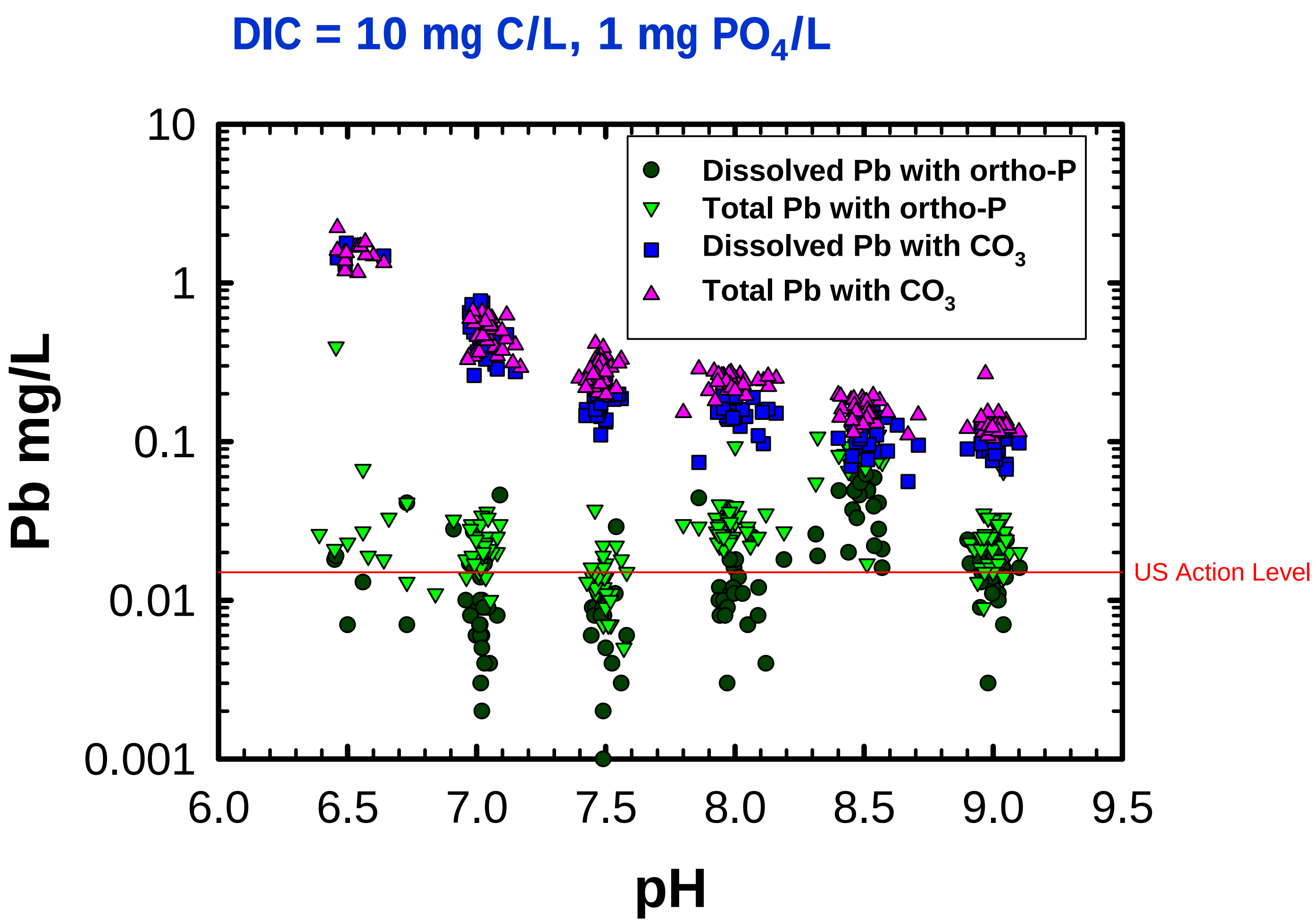
Orthophosphate Treatment for Pb(II)



- More effective with low TIC
- Lower dosages at low TIC
- pH less critical at low TIC
- Point of diminishing returns higher with high TIC

Source: Michael Schock EPA presentation to NDWAC working group

Effect of pH and PO_4 on Lead Release



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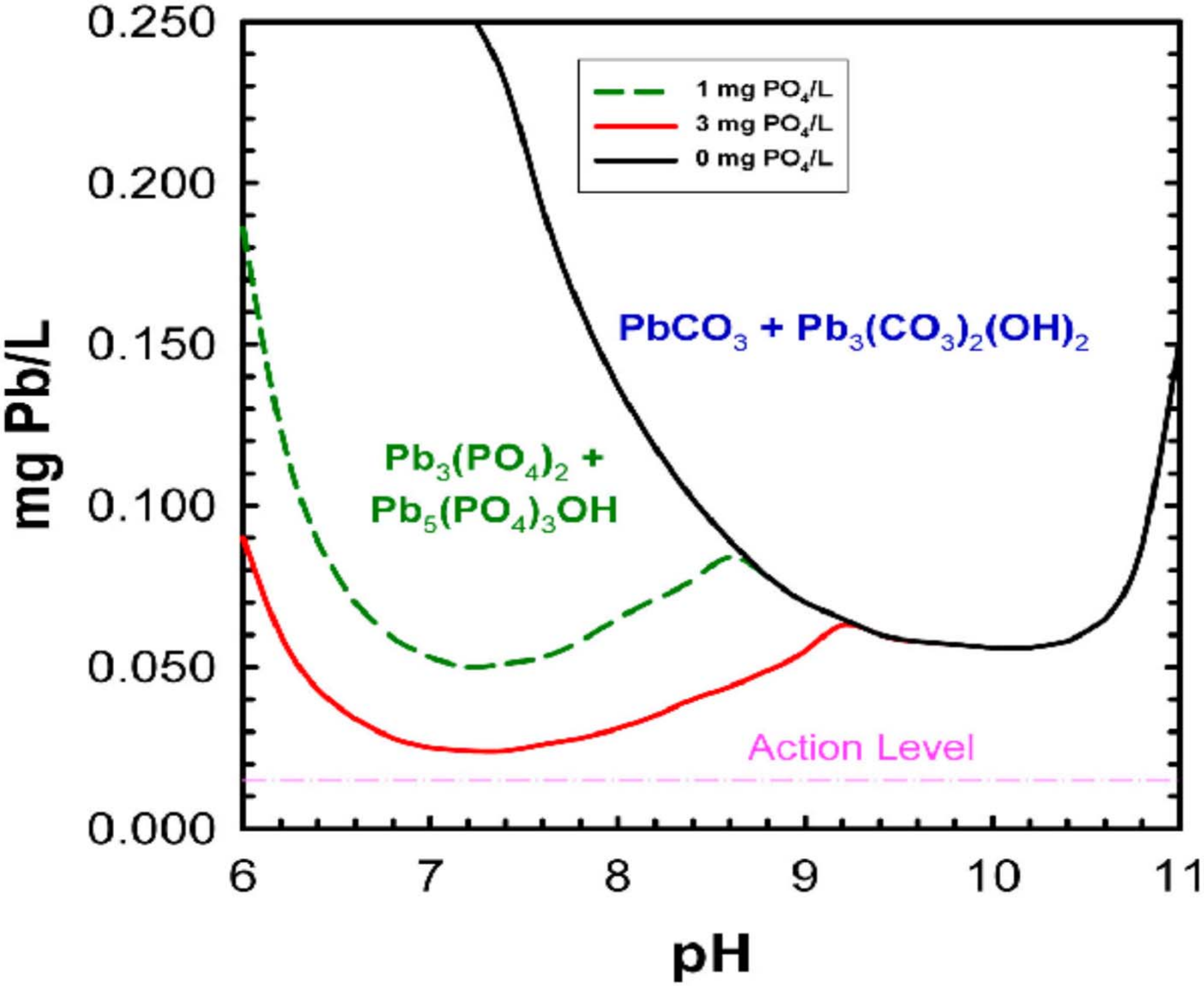


Source: Michael Schock EPA presentation to NDWAC working group

Now Let's Look at Particulate Lead

- Lead can be bound in post-treatment deposition
  - Iron
  - Manganese
  - Aluminum
  - Calcium
  - Phosphorus
- These mixed deposits are not very stable or "hard"
- Could cause erratic release of lead-rich particles
- Can create Pb buildup in interior house or building plumbing
- Maybe different in zones in a distribution system

Major Classes of Pb Pipe Deposits

- Dominantly PbO_2 Scales—these are more stable
- Dominantly Pb(II) carbonate and hydroxycarbonates—more stable
- Dominantly lead/PO4—more stable
- Surface deposits creating barriers, rich in Ca, Al, often P, with some Pb (< 20%, often 5%)-less stable
- Surface deposits rich in Fe, Mn, Al, sometimes accumulating P and Pb (< 10 %)-less stable

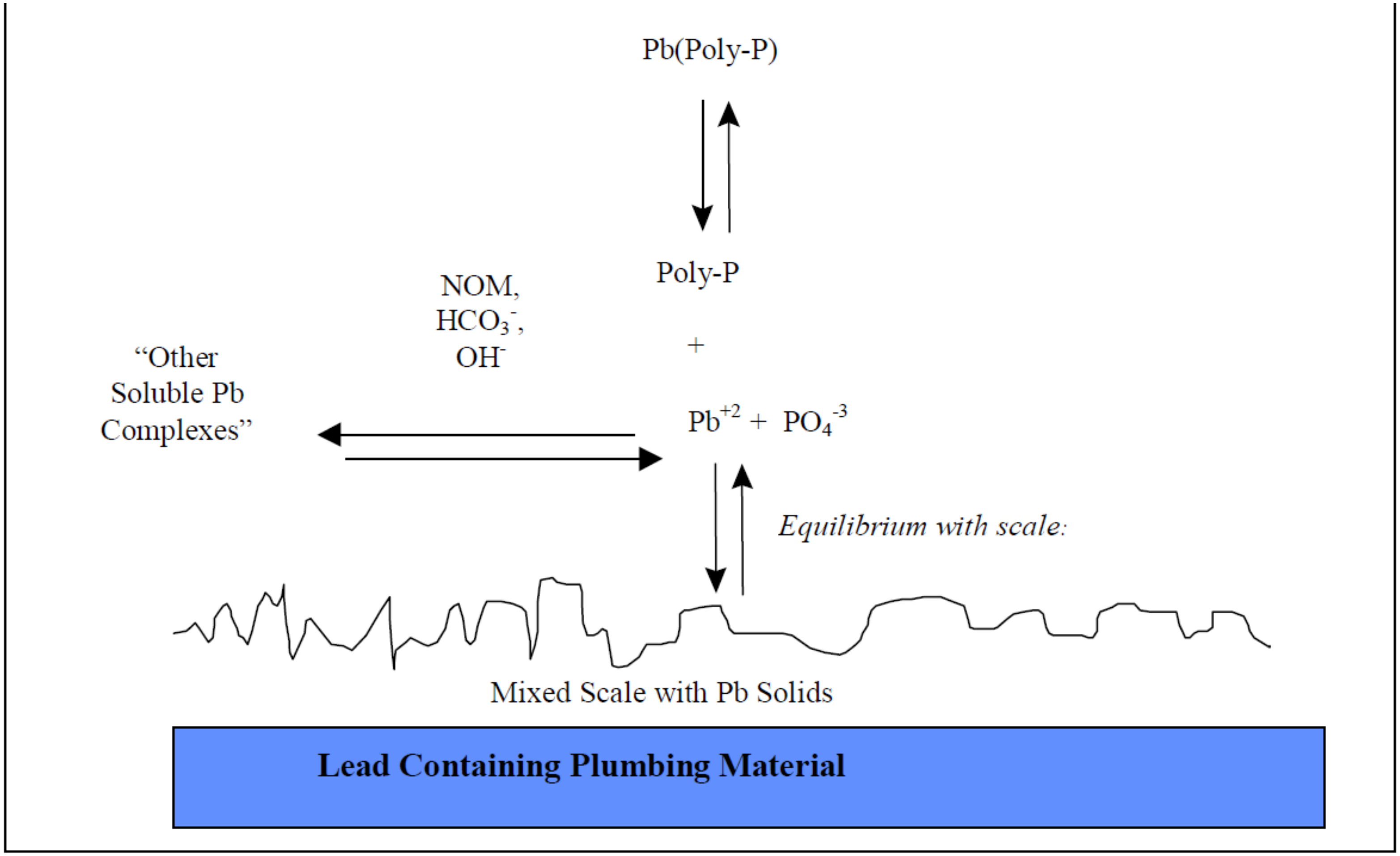
Some have Pb(II) mixed carbonate/phosphate scales

- Can cause incomplete conversion to Pb(II) phosphate phase
- Residual carbonate phase often the higher-solubility $PbCO_3$ (cerussite) form
- Blended phosphate systems rarely (to never) show crystalline Pb(II) phases

Poly and meta/hexamata phosphates

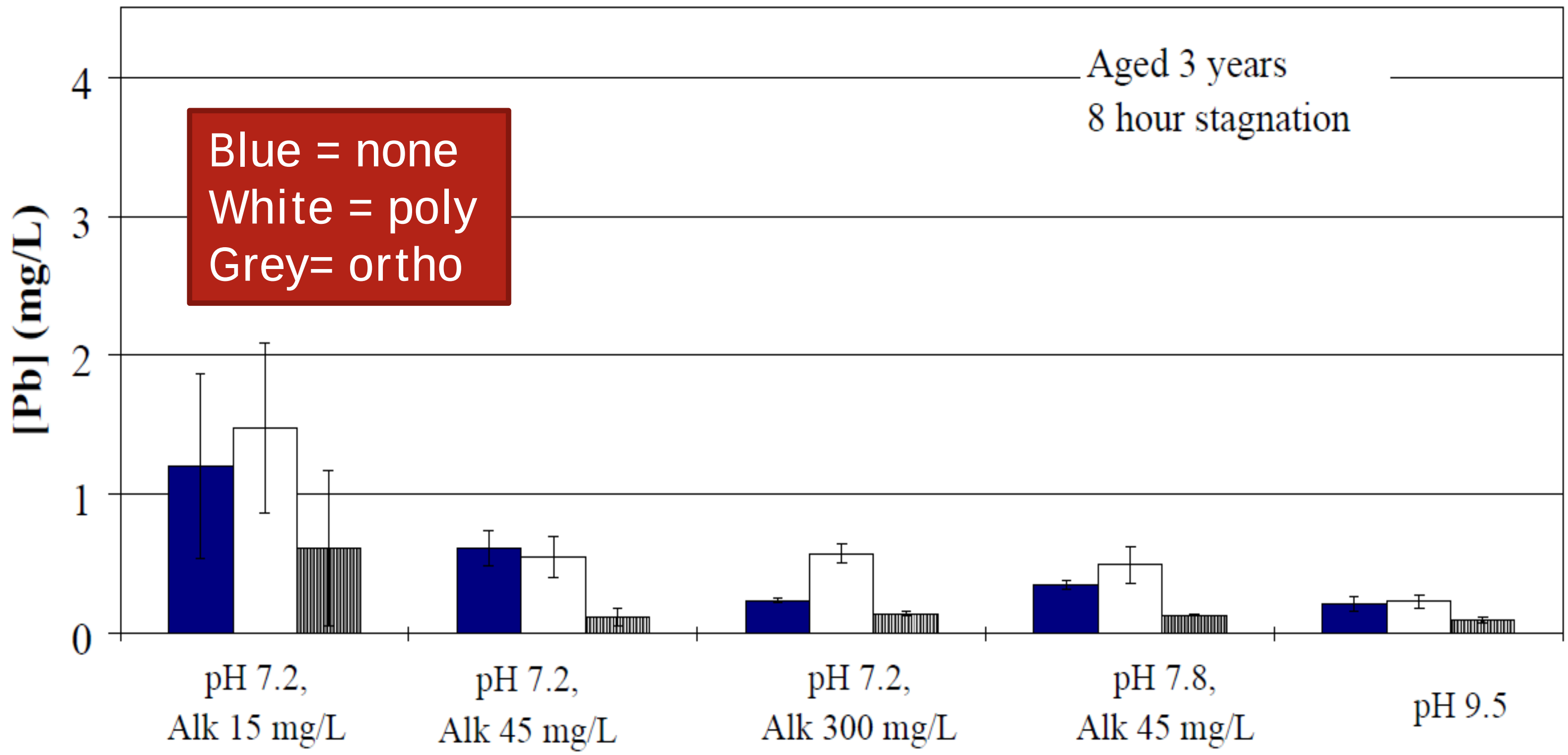
- Sequester metals so are good to minimize Fe and Mn colored water issues
- Can reduce calcium carbonate ppt
- Tend to prevent metal ppt—including lead
- React with lead to prevent Pb-ortho ppt from forming even in blended products
- Form amorphous Pb/Ca/Fe/Mn scales

Representation of Poly v Ortho P



Source: Edwards, M., and L. S. McNeill. 2002. Effect of phosphate inhibitors on lead release from pipes. *Journal AWWA* 94(1) January 2002: 79-90. **permission pending*

Orthophosphate vs Polyphosphate



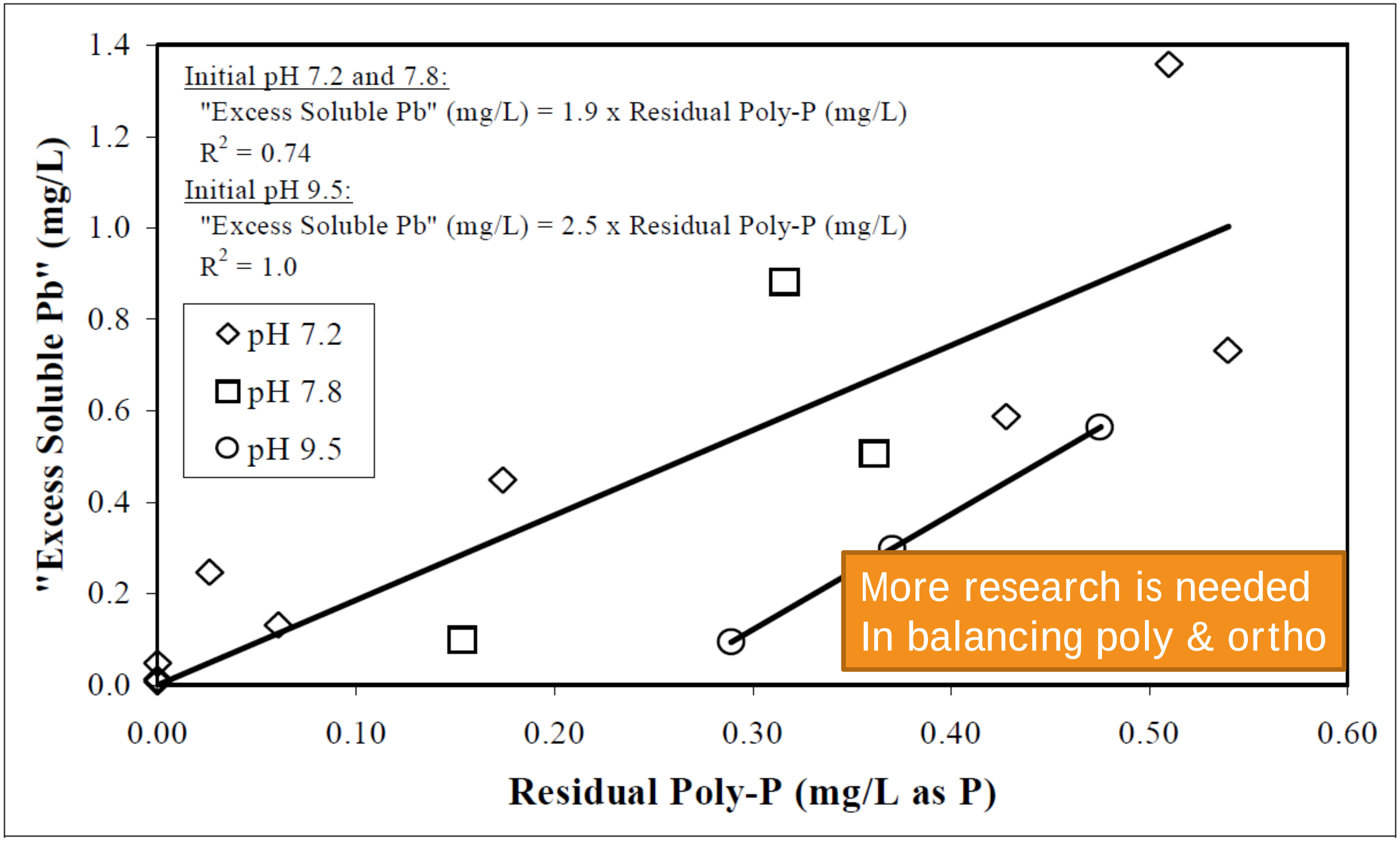
Source: Edwards, M., and L. S. McNeill. 2002. Effect of phosphate inhibitors on lead release from pipes. *Journal AWWA* 94(1) January 2002: 79–90. **permission pending*

Pb Solubility
Poly v Ortho P

Time	Control	Ortho	Poly
Time 1	1.25	0.022	1.65
Time 2	2.25	0.009	0.42

Source: Boffardi, B.P., and A.M. Sherbondy. 1991. Control of lead corrosion by chemical treatment. NACE *Corrosion* 27(12): 966–975. **permission pending*

Pb increase using Poly over Ortho P



Source: Edwards, M., and L. S. McNeill. 2002. Effect of phosphate inhibitors on lead release from pipes. *Journal AWWA* 94(1) January 2002: 79–90. **permission pending*

Ortho scales are Pb-PO4

XPS Surface Analysis on Lead for Zinc-Orthophosphate Treatment

	Atomic Concentration			
Days	Zinc	Phosphorus	Calcium	Lead
1	1.56	1.80	0.0	13.8
4	1.19	2.68	0.4	13.2
7	0.00	6.48	0.5	9.9
11	0.00	1.73	0.1	12.6
13	0.00	3.60	0.4	9.4

Poly scales are loose mixtures

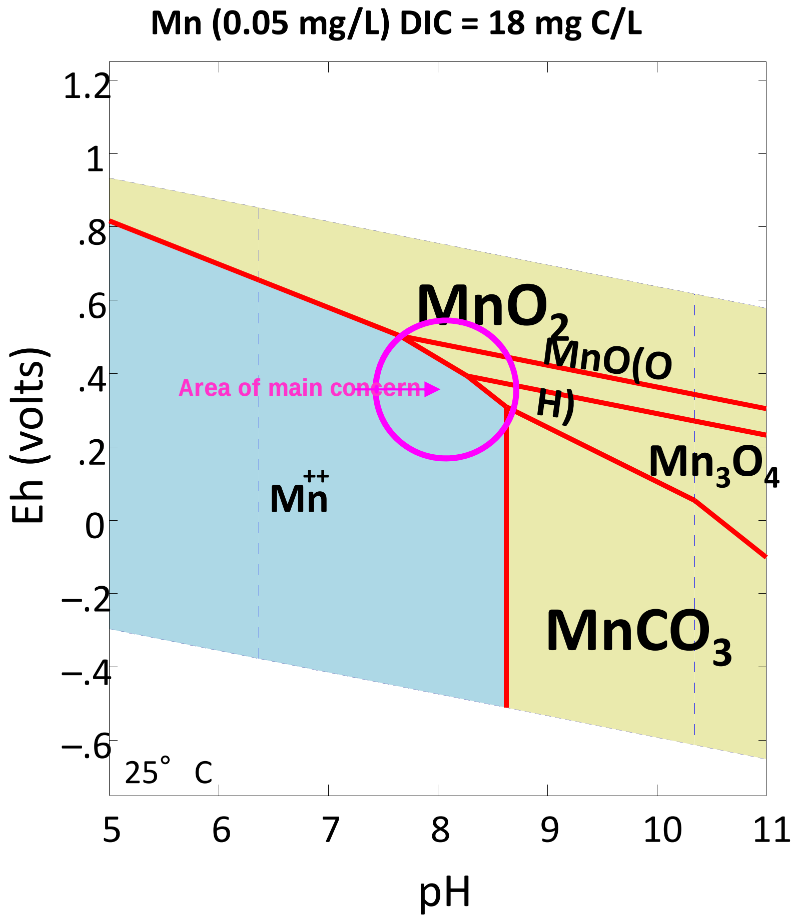
XPS Surface Analysis on Lead for Zinc-Polyphosphate Treatment

	Atomic Concentration			
Days	Zinc	Phosphorus	Calcium	Lead
1	2.74	6.60	2.3	10.9
4	5.25	7.58	3.6	9.5
7	7.55	9.17	3.8	7.0
11	7.13	7.68	3.6	6.9
13	7.46	7.44	3.3	6.3

Source: Boffardi, B.P., and A.M. Sherbondy. 1991. Control of lead corrosion by chemical treatment. NACE *Corrosion* 27(12): 966–975. **permission pending*

Changes in ORP Can Mobilize Mn, Which Then Can Carry Sorbed Pb

Example of ORP change altering Pb release



Source: Michael Schock EPA presentation to NDWAC working group

Summary of Important Pb issues

- Water quality zones in distribution system can be different
- How we sample makes a difference
- Weak scales can release lead more readily
- Particulate release—faucet velocity
- Physical disturbance risk from repairs or infrastructure renewal--PLSLR
- Low water use makes CCT of all kinds less effective
- Polyphosphate
- WQ changes effecting scales or solubility

Corrosion Control Evaluations

- Pipe loops
  - Harvest Pb pipe – keep moist
  - New Cu pipe
  - WaterRF 4317
- Coupon studies
- Desktop Studies
- Investigate potential for microbial growth w/ orthophosphate
  - Limiting nutrient assessment (C:N:P)
- Systems with Galvanic Corrosion
  - Benchtop laboratory study or pipe loop

WaterRF 4317
Corrosion Evaluation Rig

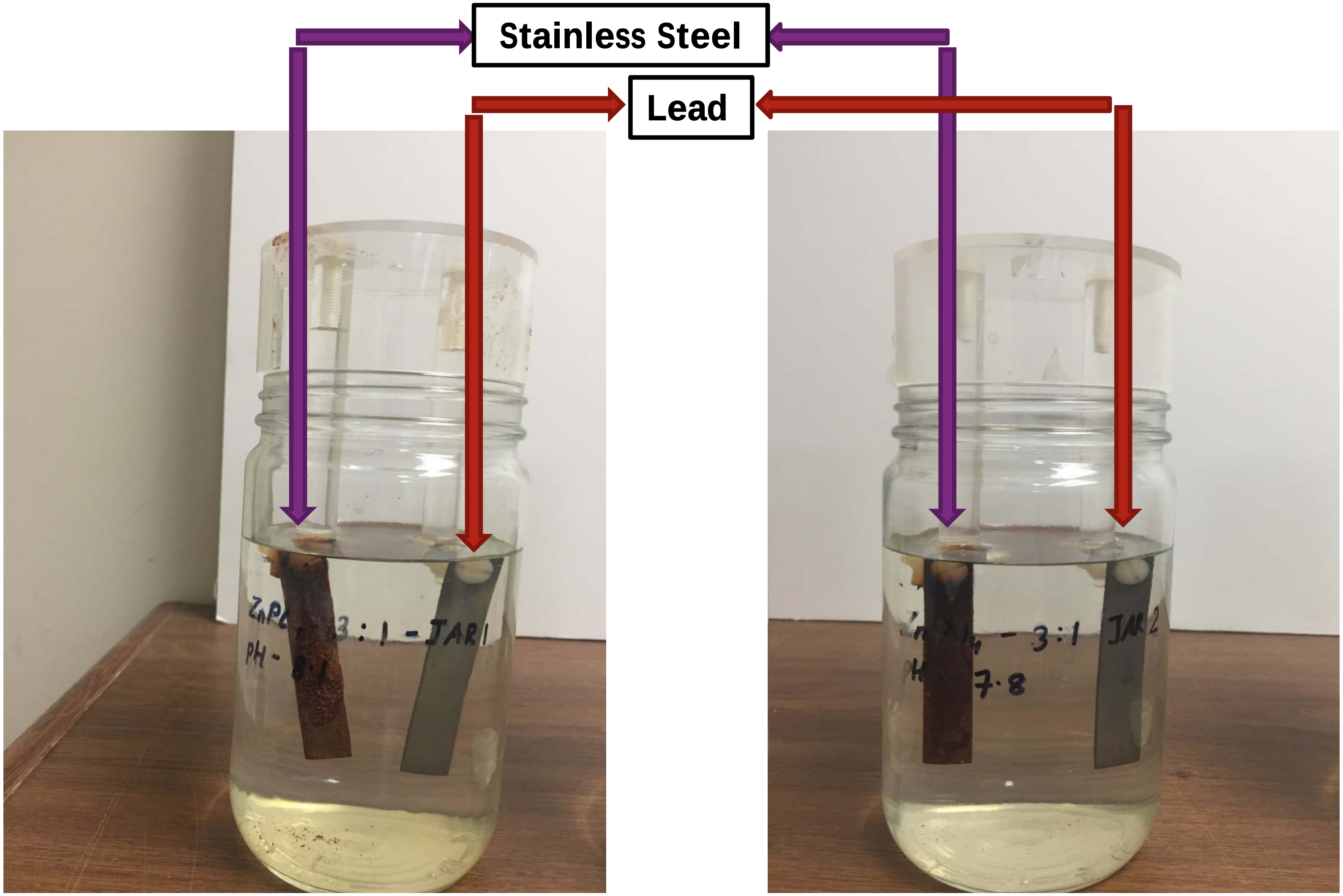
Frame is:

- 103.25 in length,
- 26 in width,
- 48 in height

Source:

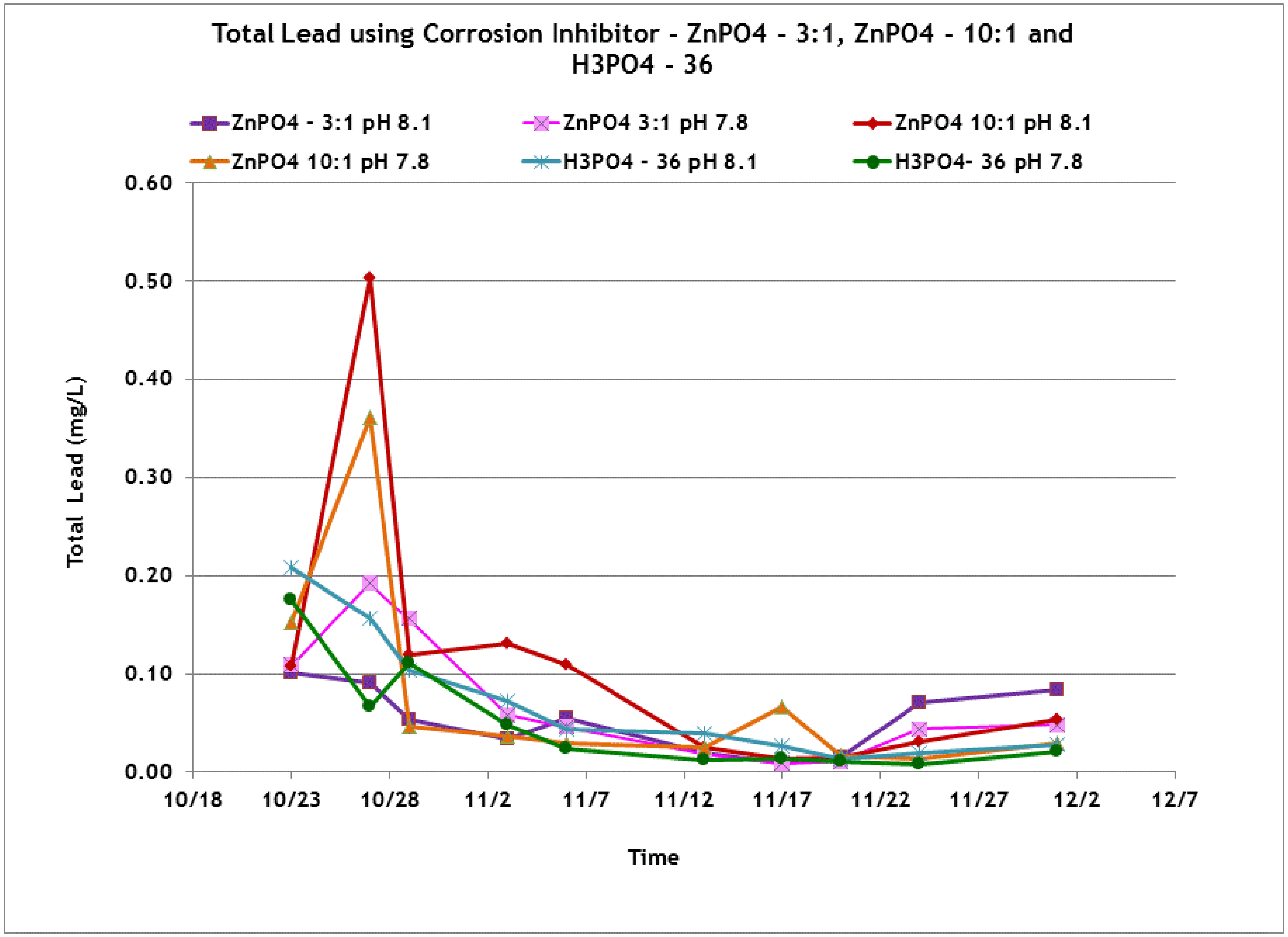
Edwards, M., P. Scardina, J. Parks, and A. Atassi. 2011. Non-Intrusive Methodology for Assessing Lead and Copper Corrosion (Water Research Foundation Project 4317): Installation and Operation Manual for Corrosion Evaluation Rig – Revision 2 (October 26, 2011).

Coupon Study at EE&T: ZnPO4 (3:1)



Example Coupon Result

EE&T, 2015 Study



Results are relative but coupon studies can be very effective tools

Which OWQP are typically monitored?

pH, alkalinity, T, Ca, conductivity, silica (if required) and phosphate (if required).

How were the monitoring data used?

Typically reviewed by District Engineers by hand to determine that the system is maintaining treatment. Typically not kept in database.

Example Required WQP

System	Corrosion strategy	Required WQP	Treatment goal
A	pH and alk adjust	Min pH 9.0 in DS Min alk 37 mg/L	Min pH 9.3 Min alk 40 mg/L
B	pH and alk adjust	Min pH 7,5 Min alk 15 mg/L	pH 7.7 - 7.8 Alk >15 mg/L
C source 1 source 2	pH and alk adjust	Min pH 8.0 EP Min pH 8.8 EP	pH 8.6 (source 1) pH 9.2 (source 2)

Source: Cornwell, D., R. Brown, and N. McTigue. 2015. Controlling lead and copper rule water quality parameters. *Journal AWWA* 107(2) February 2015: E86–E96. **permission pending*

Example Required WQP

System	Corrosion strategy	Required WQP	Treatment goal
D	Phosphate addition, pH adjust	pH > 6.8 <8.2 PO_4 range 1.0 - 4.0 mg/L	pH 7.2 PO_4 2 mg/L
E	Phosphate addition, pH adjust	Min pH 7.2 Dis PO_4 range 0.5 - 5.0 mg/L	pH > 7.4 < 8.0 PO_4 1.0 – 4.5 mg/L
F source 1, 2, 3	Phosphate addition	PO_4 range 1 - 2.0 mg/L pH range 6.5 - 7.9	pH 7.1 EP pH 6.9 DS $ZnPO_4$ 1.5 mg/L Zn 0.12 mg/L

Source: Cornwell, D., R. Brown, and N. McTigue. 2015. Controlling lead and copper rule water quality parameters. *Journal AWWA* 107(2) February 2015: E86–E96. **permission pending*

How Should We Rethink WQPs

- What should we monitor for and goals
- Where should we monitor
- How frequently should we take samples
- How should we analyze the data

What Should We Monitor for

- Larger utilities might consider pipe scale analysis to help define WQPs
- Certainly pH, Alkalinity, P if used
- Need Consider
  - ORP
  - Cl2/NH2CL
  - Fe, Mn, Al
  - Cl/SO_4 ratio

Control Charts

- WaterRF 4286
  - Distribution System Water Quality Control Demonstration
  - Process Research Solutions, LLC
  - This chart uses single data and means
  - EE&T prefers Grouped data and medians

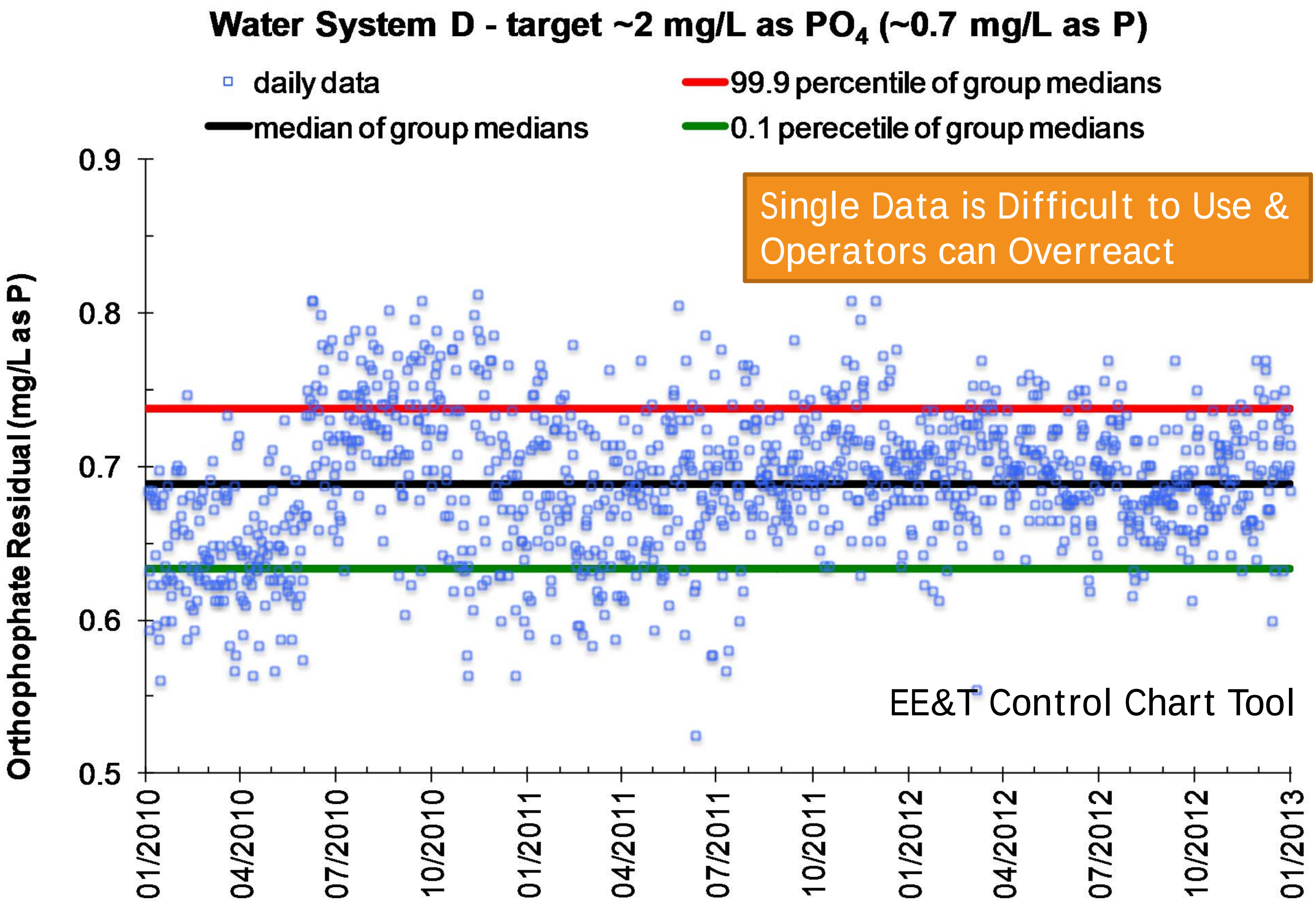
- “Out of Control” “In Control”
  - Control chart terms—not a regulatory statement
  - Out of control indicates room for operator improvement in reducing variability
  - The better the chemicals are controlled the tighter the band gets

Group Data Approach

- Doesn’t use individual data – uses statistical sub sets (“bins”)
- Can use median or mean
- Uses Control Limits for median or mean
- But median values eliminate outliers
- Follows original Shewhart control charts for process control
- Upper limits (UCL) and lower limits (LCL) are based on a 3 sigma range
- **Control charts are not compliance values**– they are for process optimization and control

Example Individual Data

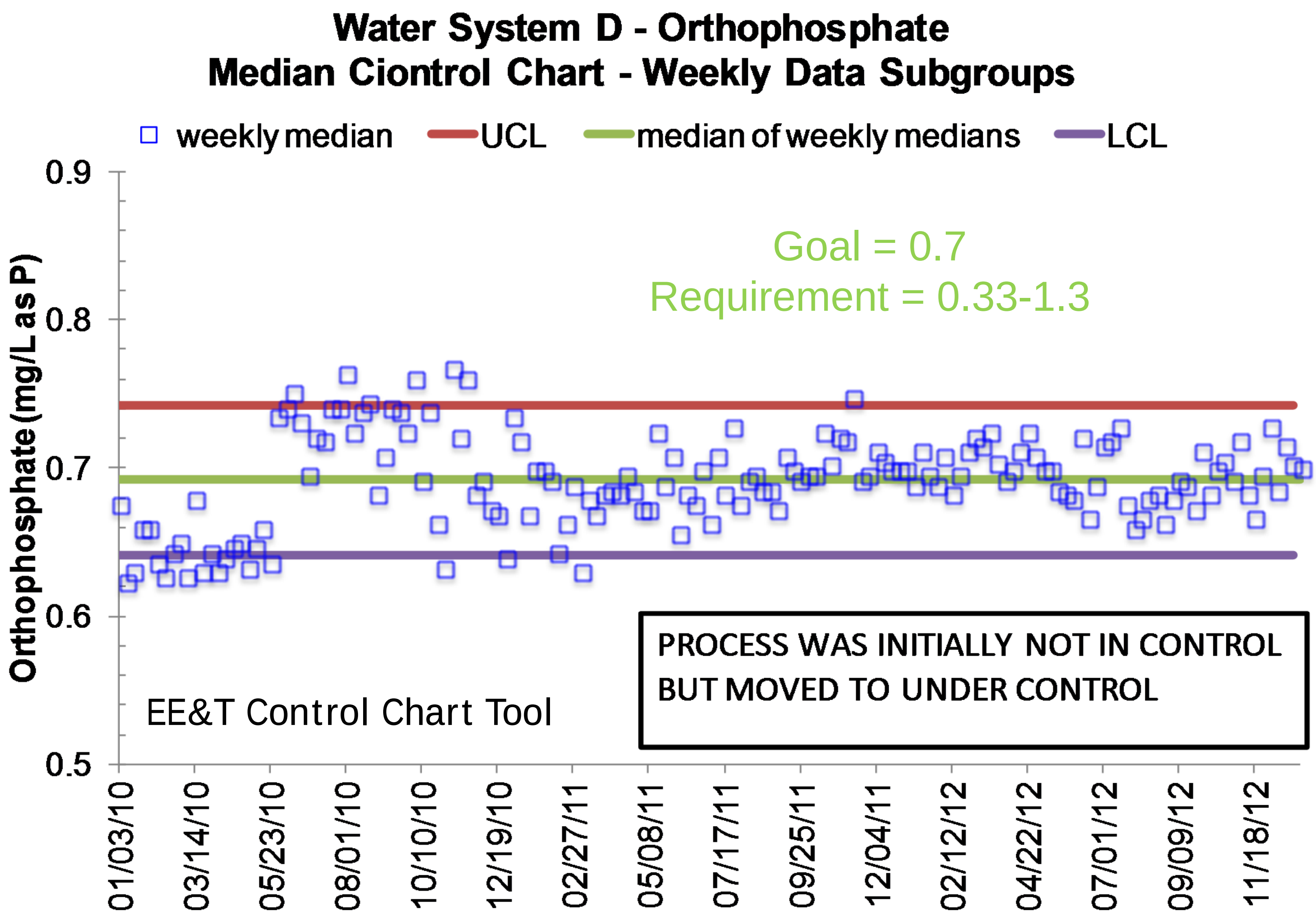
- Next Graph shows individual PO_4-P Data
  - Operator would be reacting to data changes that are beyond operations control
  - Over-reaction can be worse than no reaction
  - Contrast with subsequent graph on using statistics of data subsets for control charts



Source: Cornwell, D., R. Brown, and N. McTigue. 2015. Controlling lead and copper rule water quality parameters. *Journal AWWA* 107(2) February 2015: E86–E96. **permission pending*

Example Grouped Data

- Next Graph shows same data grouped in 1-week bins
- Operator now can easily see trends in the plants control of phosphate dose over time
  - Operations can react to first low data trends seen in the plot and then high data trends seen
  - Changes can be made slowly without over reacting
  - Over time variability will be reduced and the upper/lower control lines will come closer together over time



Source: Cornwell, D., R. Brown, and N. McTigue. 2015. Controlling lead and copper rule water quality parameters. *Journal AWWA* 107(2) February 2015: E86–E96. **permission pending*

Welcome to the Environmental Engineering and Technology Control Chart Tool

| EE&T, Inc.

ENVIRONMENTAL ENGINEERING & TECHNOLOGY, INC.

(757) 873-1534 www.eetinc.com

A tool designed for utilities to evaluate and control water quality parameters, including Lead and Copper Rule WQPs

What is a Control Chart?

How to use the Tool (Video)

Get Started!

We Have a Lot To Do But Who Better Than Our Professionals in Water