



Office of Research and Development

# Lead and Copper Treatment: Back to the Basics

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- Miguel Del Toral, USEPA Region 5

## Disclaimer

*This presentation has been reviewed in accordance with U.S. Environmental Protection Agency (EPA) policy and approved for external presentation. The views expressed are those of the author[s] and do not necessarily represent the views or policies of EPA.*



## “Corrosion Control” Treatment is Intertwined with All Treatments Affecting DS Water Chemistry

**To achieve OCCT, overall process control and distribution system water quality optimization must also be achieved. OCCT is not an independent, separate process.**



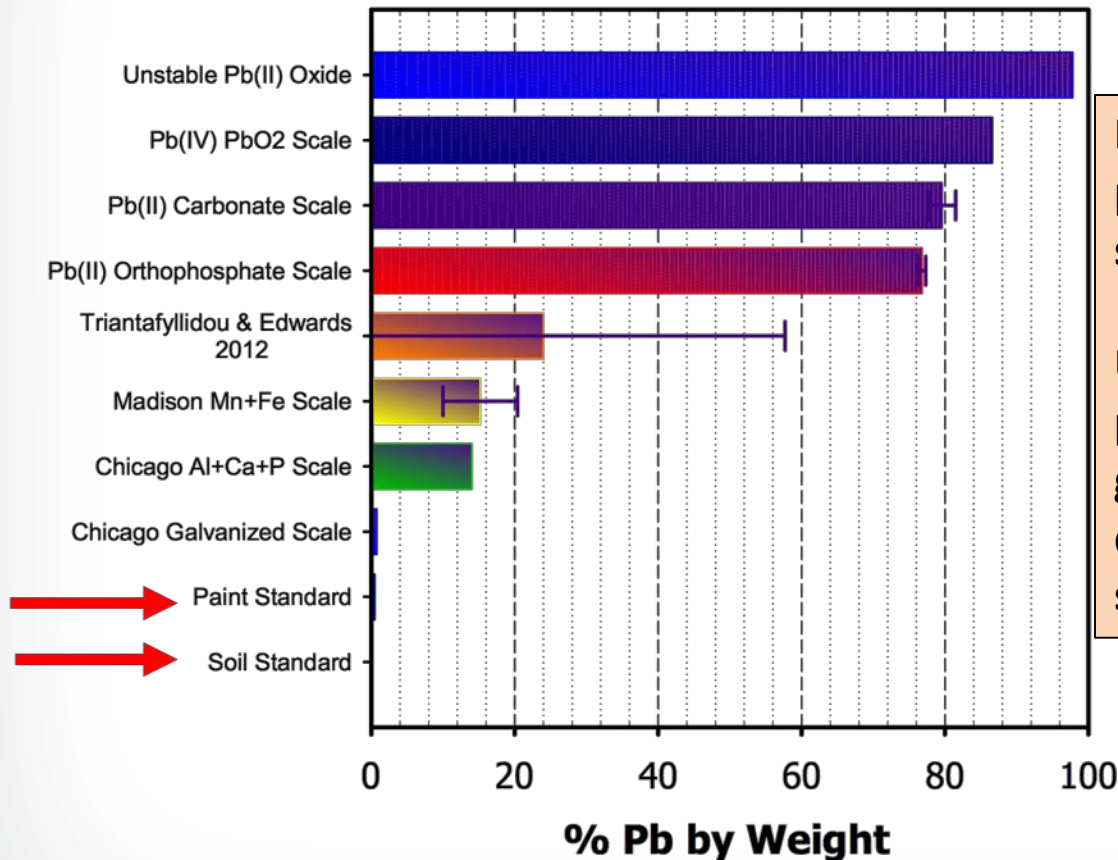
Not Just Diamonds! Lead Pipes are Forever...

## Lead Pipes Won't Go Away Any Time Soon

Installed Right After the Civil War in Cincinnati: Any Signs of Failure *after 150 Years?*



# Pipe Scale Particles Have More Lead Than Pb in Paint, Soil, or Hazardous Waste



Erosion and suspension of particles from pipe corrosion scales and deposits is inevitable.

Untimely release of small particles can potentially result in greater relative exposure from drinking water than paint or soils

Drinking through Lead-Painted Straws

- Typically “disequilibrium” chemistry in 1st liter
- Lead solder corrosion complex function of water quality
  - Lead migration is by galvanic corrosion of copper joint with lead solder
  - Mitigation of solder corrosion may differ from control of simple plumbosolvency
- Leaded brass corrosion varies with water chemistry and time
  - In many or most waters, the internal galvanic coupling of the copper and lead may result in preferential lead oxidation
  - Brass fittings often connected to lead or copper pipes and also prone to galvanic corrosion and dealloying





## Times (and Science) Have Changed

“Wish I didn't know now what I didn't know then”

-Bob Seger (1980)

- 349 Lead pipe samples, plus assortment of galvanized, Cu, others
- 63 systems from USA & Canada (plus 1 from France)
- 22 have X-ray amorphous outer layers
- 10 of the 22 are from “pH/alkalinity” systems



## There Are Many Types of Scale on Pb Pipe

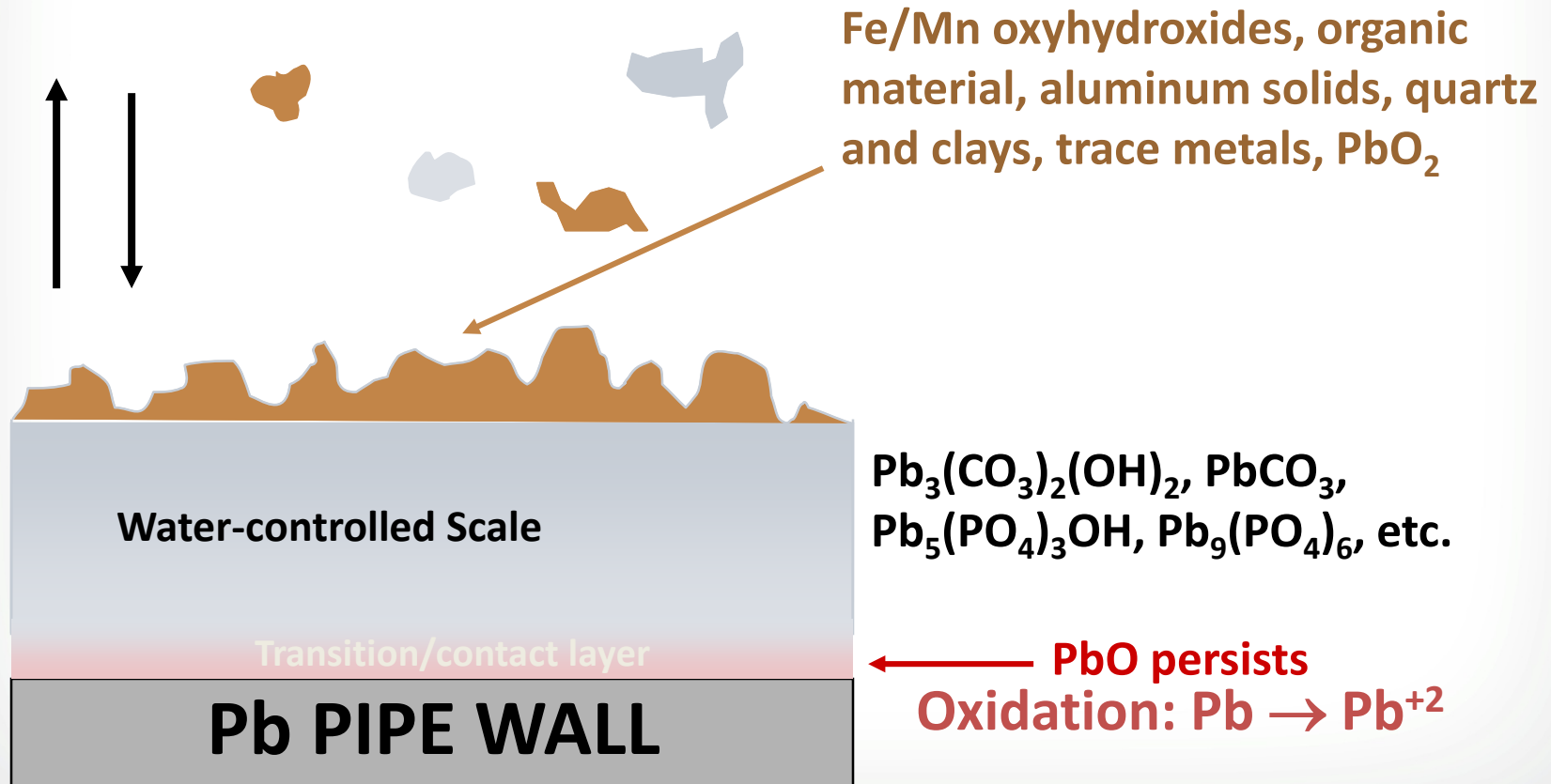
- Simple carbonate or hydroxycarbonate Pb(II) mineral
- Simple Pb(II) orthophosphate mineral
- Simple PbO<sub>2</sub> solid phase, by itself or mixed with Pb(II) phases
- Mix of Pb(II) phases
- **Protective “diffusion barrier” materials**
  - Could be insoluble amorphous Pb(II) phase
  - Adherent non-Pb phase, with some Pb in it
- **Surface fouling deposit**
  - Primarily not made of lead, usually not crystalline
  - Lead may sorb to surface
  - Often not adherent



# Conventional Pb(II) Deposit Schematic

(Exaggerated vertical scale!)

Soluble  
Metal



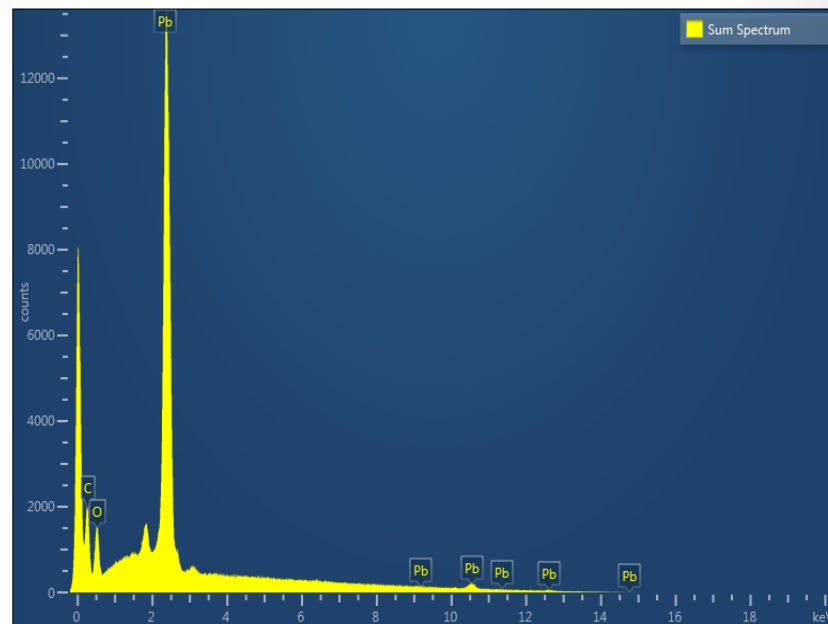
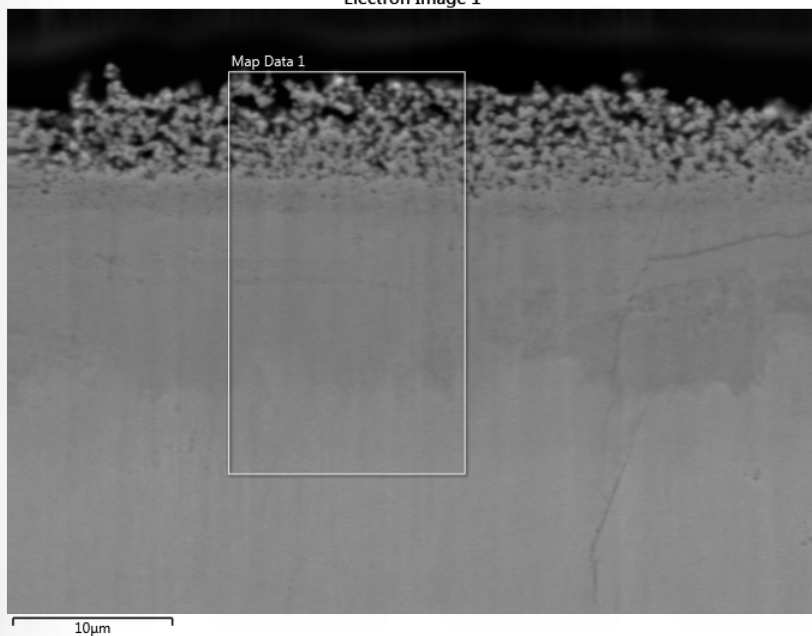


# Nothing but Pb's and O's

OHCIGRA2-Pb

2/7/2012

Electron Image 1

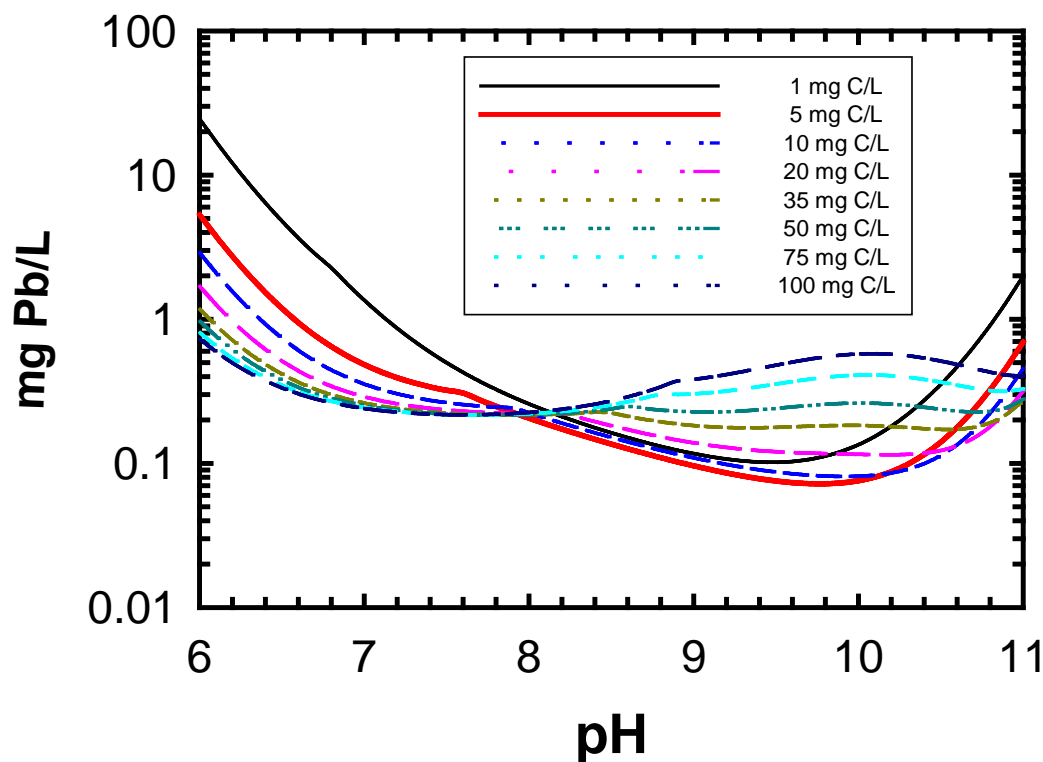




## Simple “Carbonate Passivation”

### Low DIC/High pH Strategy More Difficult with LSLs than Lead Solder or Brass

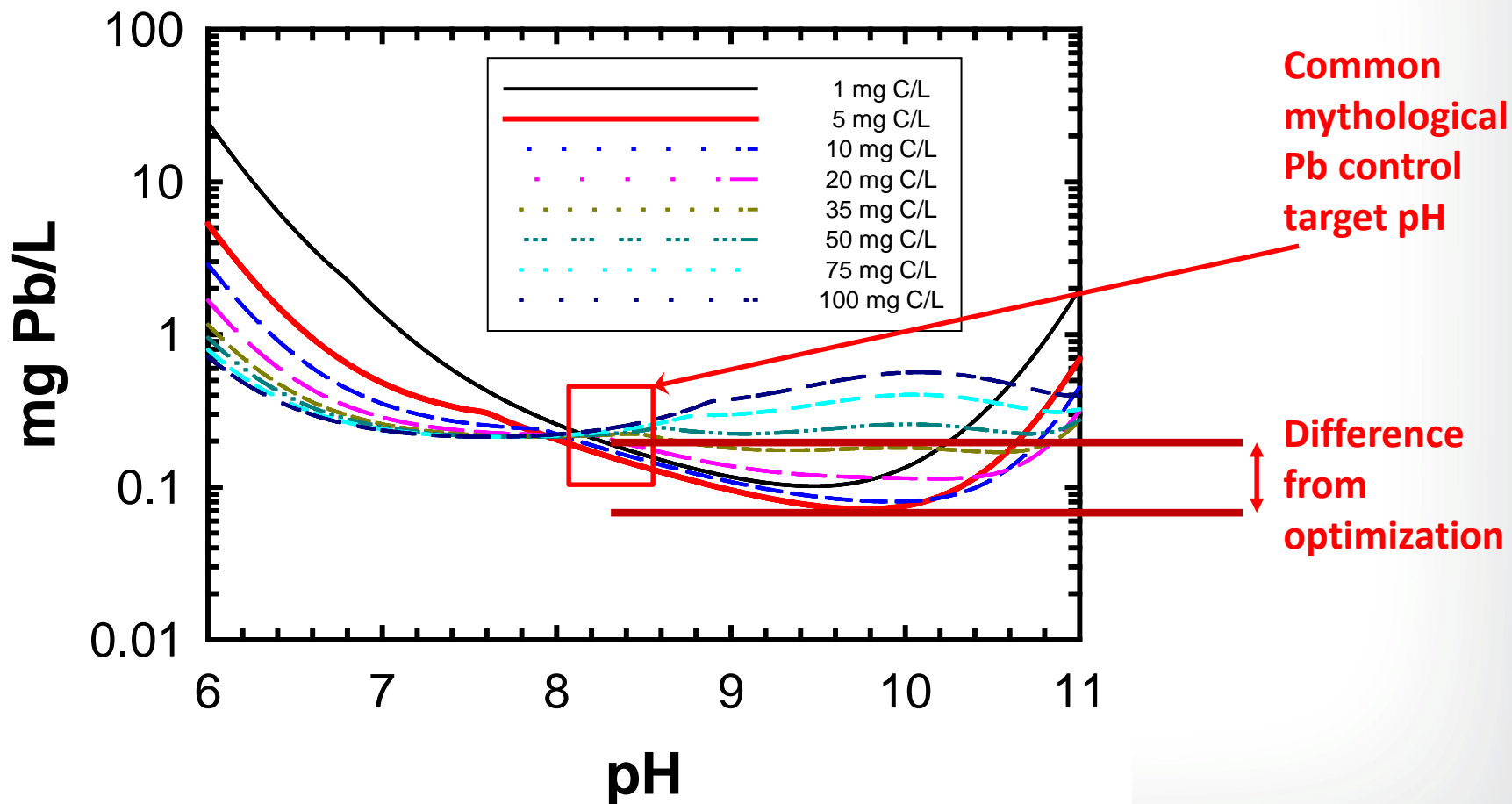
- The first formed solids with major treatment change.
- It is only possible to nearly minimize Pb levels at pH >> 9. Can only work in “soft” waters.
- Likely never as good as  $\text{PbO}_2$  or orthophosphate
- Formation of Pb(II) carbonate or hydroxycarbonate much faster than formation rate of Pb(II) orthophosphate films
- Formation of Pb(II) hydroxycarbonate solid is a precursor to the formation of less-soluble protective films of either Pb(II) orthophosphates or  $\text{PbO}_2$

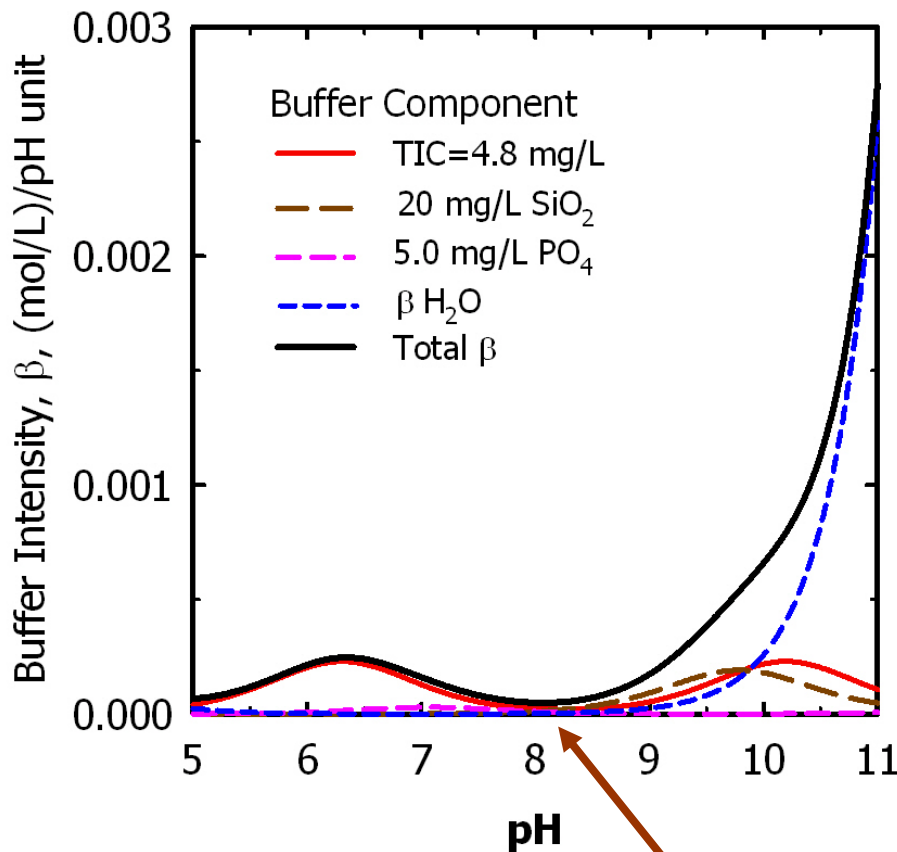




## Simple “Carbonate Passivation”

Ineffectiveness of carbonate passivation in LSLs is hidden by first-liter sampling





Carbonate is almost always most important unless low DIC and high inhibitor doses.

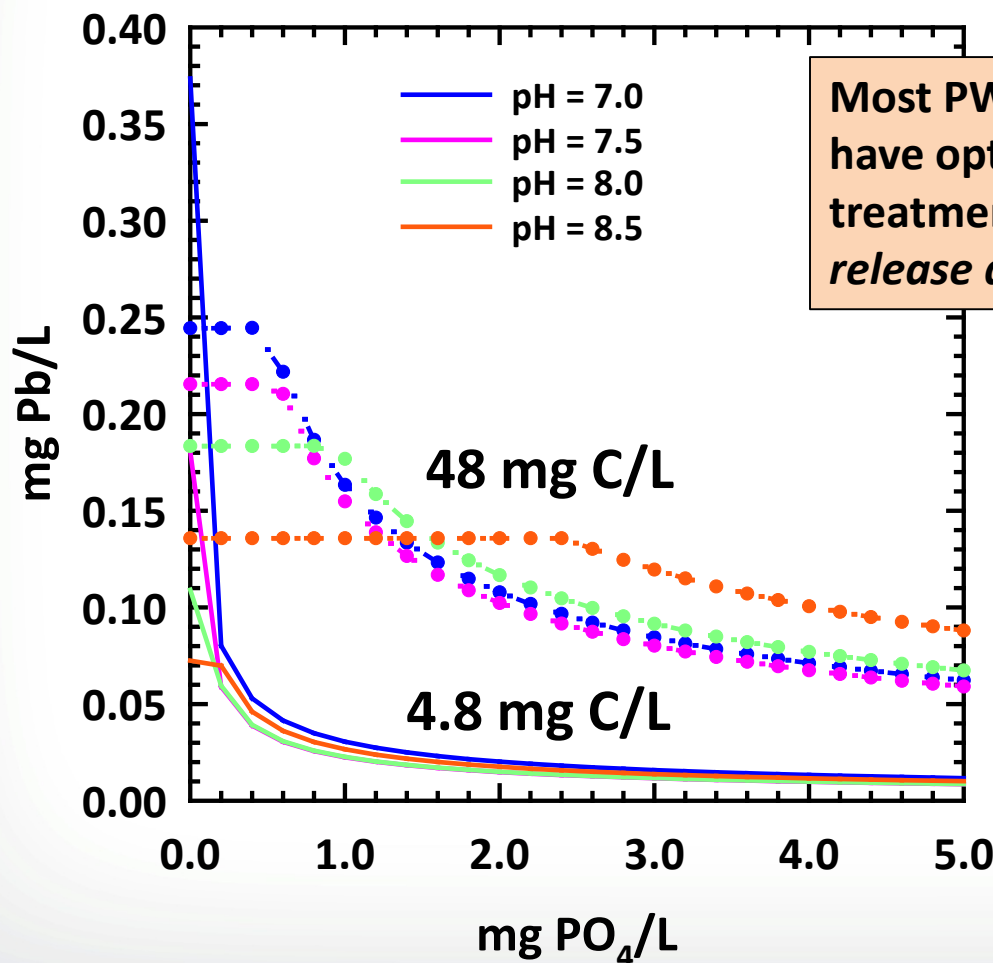
Keep away from this pH zone:  
Unstable pH!

## [Seemingly] New Ideas on pH/DIC Relation to Orthophosphate Dosing



“Point of Diminishing Returns” is key to cost-effective lead release control and exposure reduction, if secondary interferences are removed

## Effectiveness Depends on Dose, DIC, pH and “Cleanliness” of Pipe Surface



Most PWSs with LSLs currently do not have optimized corrosion control treatment *in terms of minimizing Pb release and exposure.*

- pH less critical at low TIC
- pH less critical at high PO<sub>4</sub>
- Point of diminishing returns higher with high TIC
- Faster Pb reduction at high PO<sub>4</sub>

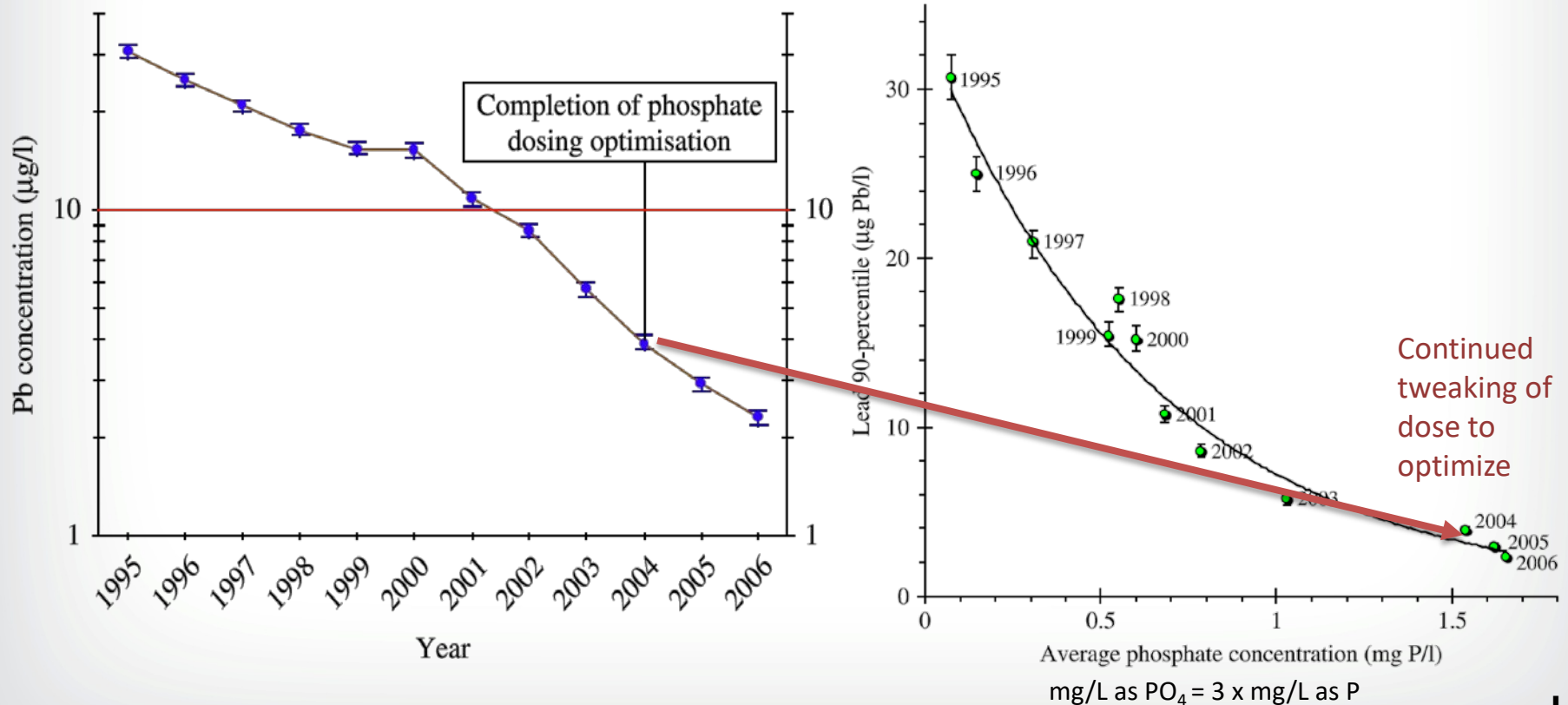
Typical UK Dosages: 4-6 mg/L





# Treatment Works on Both Soluble & Particulate Release

**Aggregated UK Monitoring Data:** Used two-pronged approach:  
(1) Initial dose estimation by pipe rig study for background water  
(2) RDT tap monitoring to assess progress & exposure

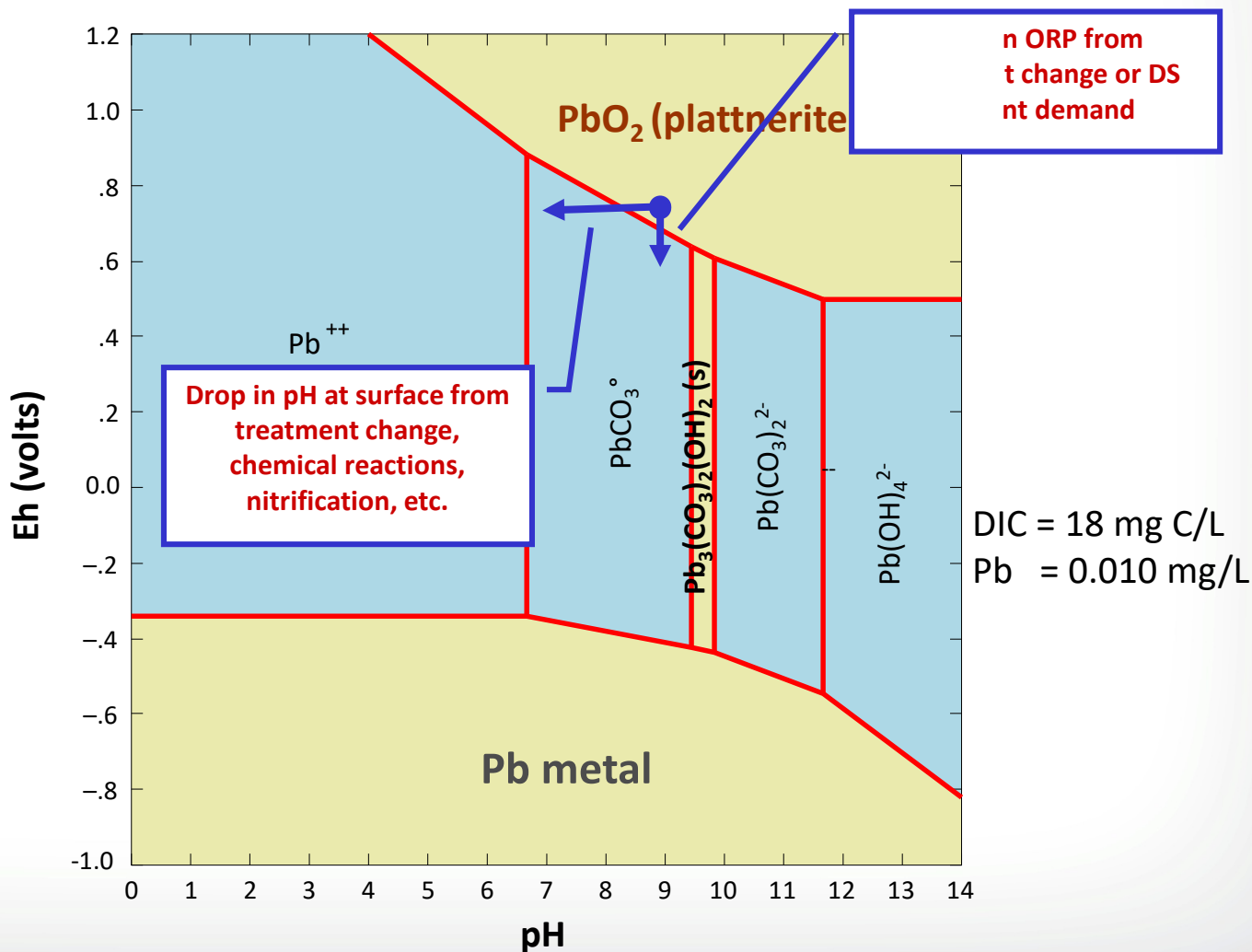


- Large fraction of US water systems do NOT have simple Pb(II) orthophosphate scales, so theoretical graph does not apply
- PODR may relate to other background chemistry factors
  - Ca, Al, Mg, Fe, Mn
  - Amount and type of P, Si
  - Other constituents (including NOM, chlorine, chloride)
- Physical properties of barrier films are best determined by sampling under normal household usage conditions
- Susceptibility to physical/hydraulic disturbance or flow is likely to vary across deposits



## Chemical Changes Cause Dissolution of $\text{PbO}_2$

Disinfectant demand in DS must be controlled and enough free chlorine consistently maintained throughout LSL area

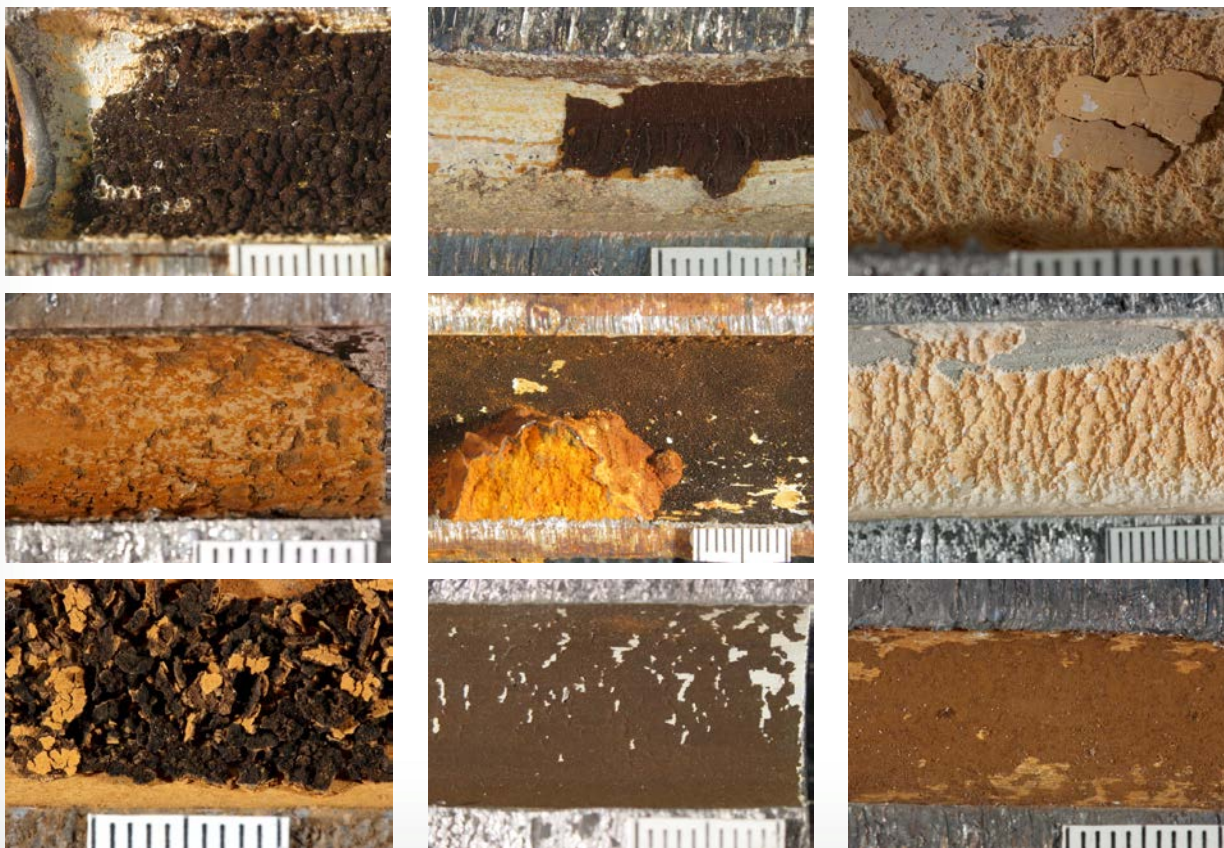


# Significant non-Pb Scale Components



May be more prevalent than “normal”  
lead solids across all systems

22 of 63 DWDS studied by EPA show external layer deposits almost completely made of poorly crystalline Mn, Fe, Al, Ca, or Si-rich phases



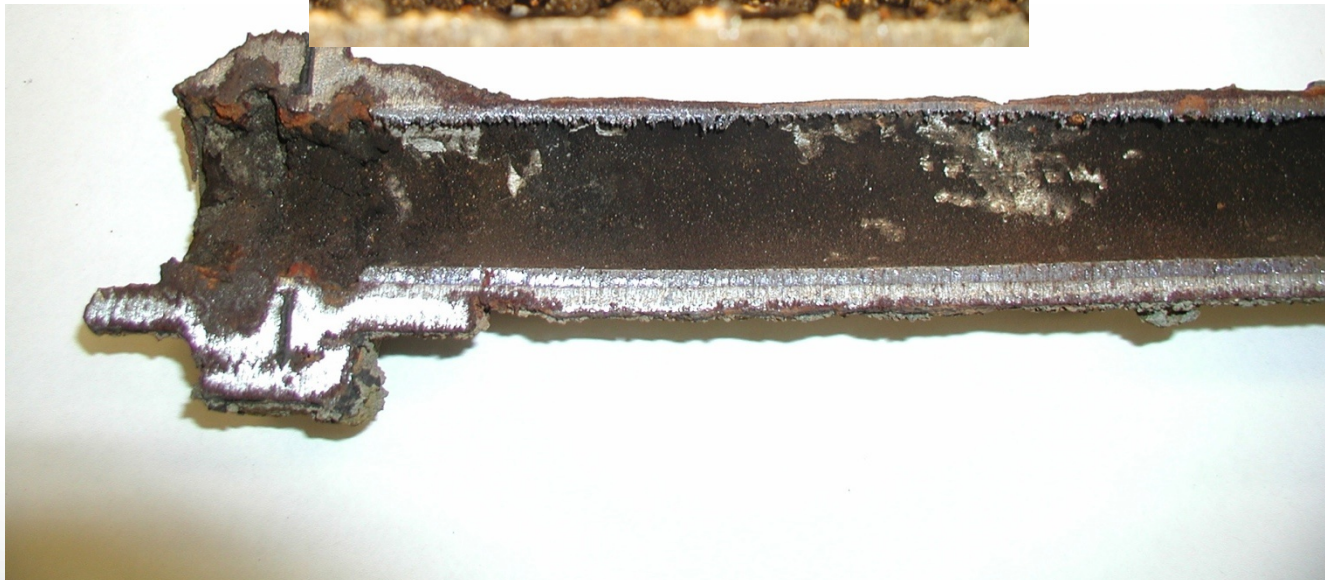
Adding orthophosphate or just adjusting pH with thick coatings likely will not minimize lead release until causes of the interfering buildups are controlled



# Mn-Rich Surface Material on Pb Pipe



**Highly detrimental to effectiveness of any CCT strategy & promotes particulate release**



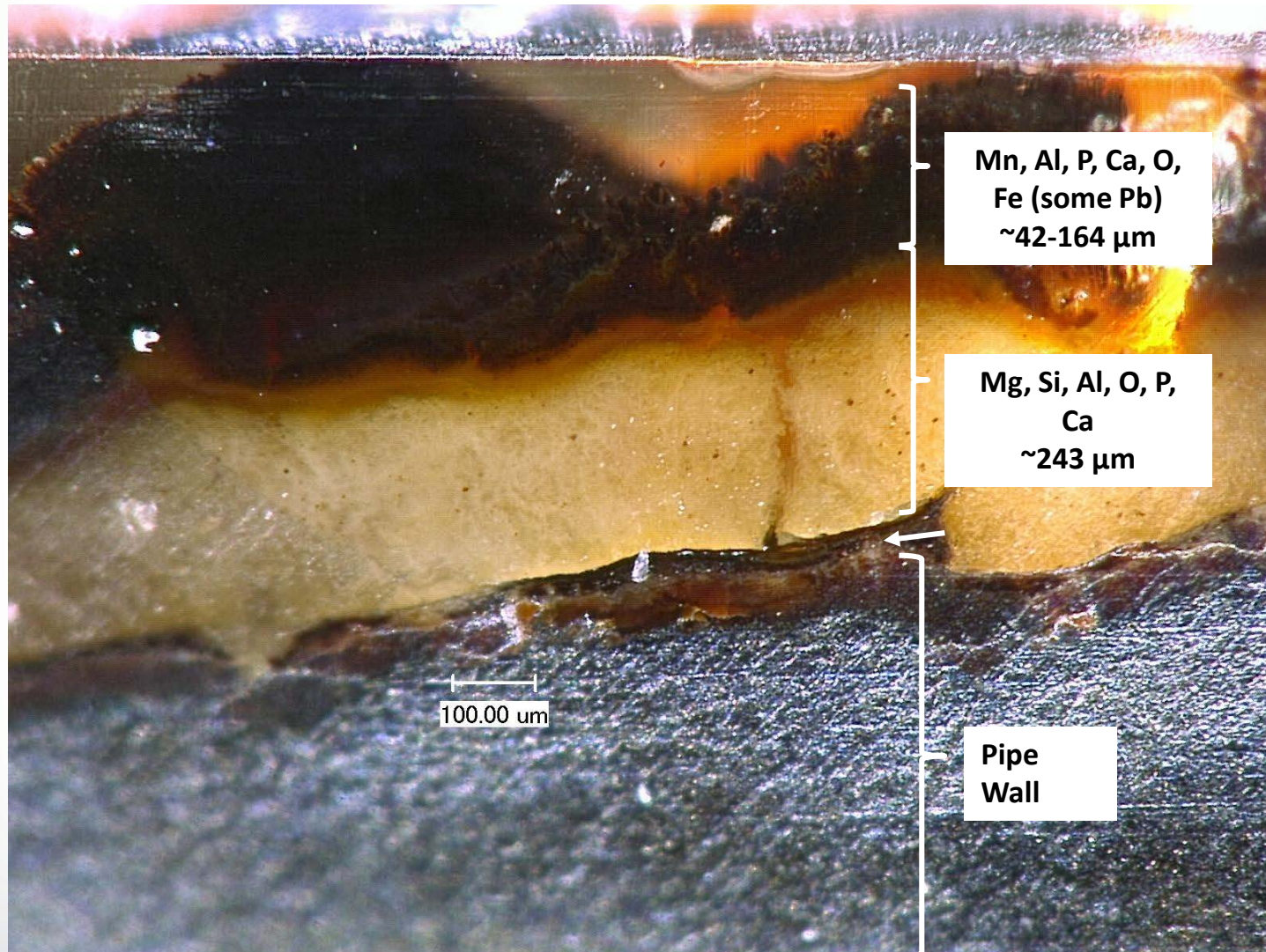


## Representative of Barrier Film Scale

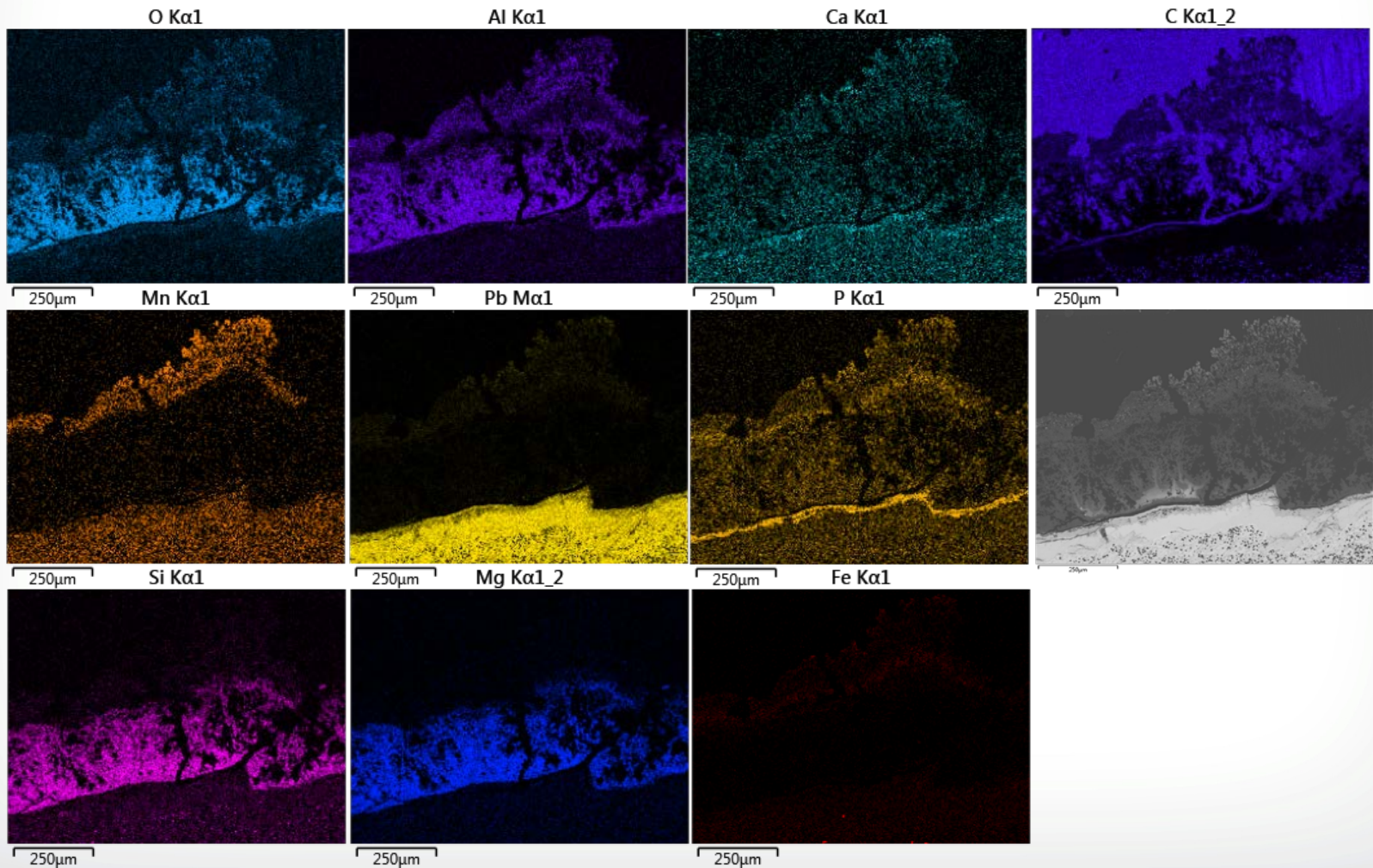




# Common P-Treated Scale Morphology



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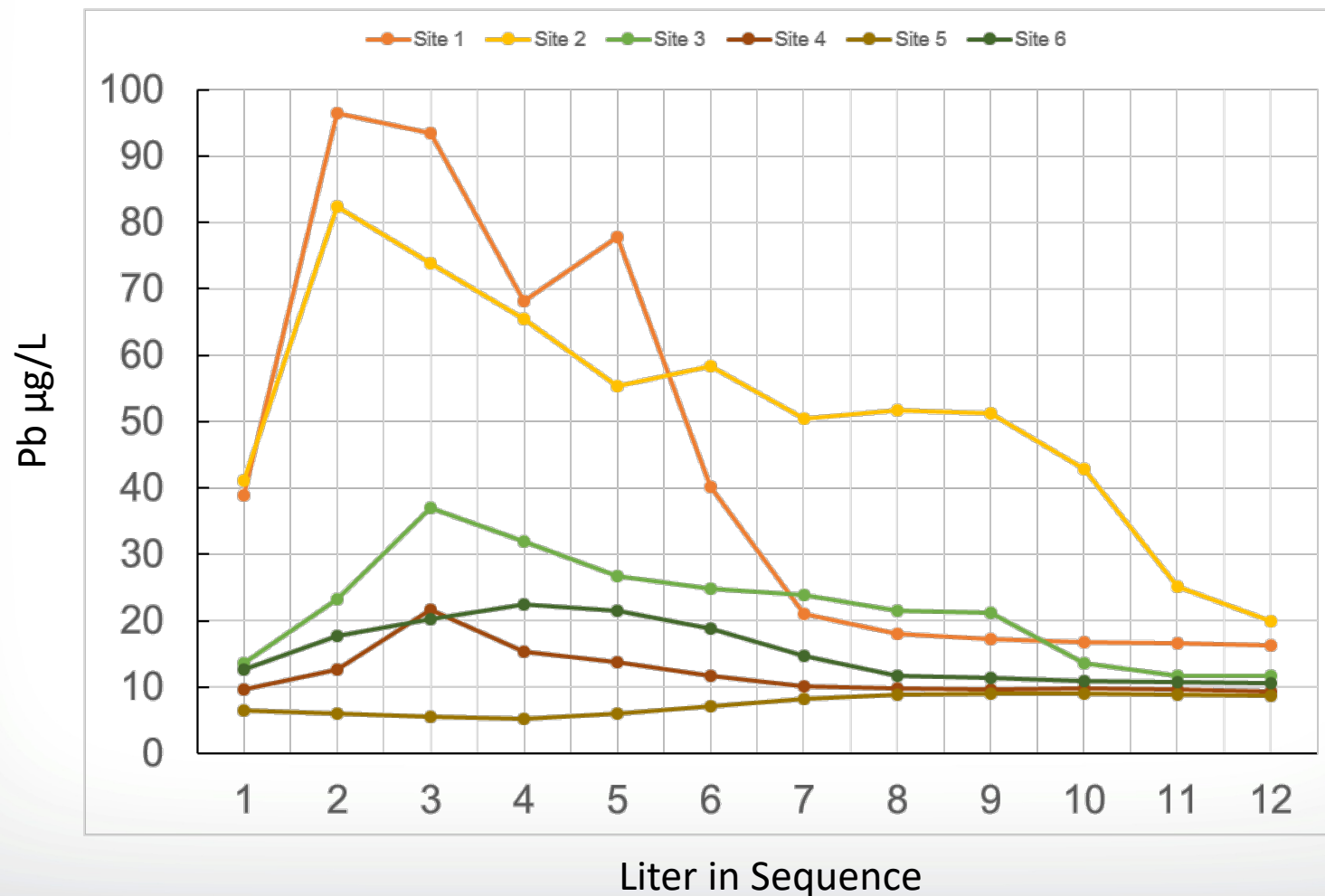






# Pb Profiles in System with Al-Si-Ca Rich Deposit

< 10% Pb in surface scale, no crystalline Pb phases at surface





## Blended Phosphates Do Not Fit Orthophosphate Predictions

Not Forming Simple Pb(II) Orthophosphate Solids

Sample ID	Layer	Al	Ca	Fe	P	Pb	Zn
Pb-A & Pb-B Average	1	16	7	1.9	11	14	0
	2	12	4	0.5	6	39	0
	3	4.8	1	0.4	2.1	62	0
	4	0.4	0	0.1	0.2	80	0
G	1	4.2	1	31	2.7	0.8	22
	2	0.5	1	57	0.2	0.1	5.8
	3	0.6	0	56	0.1	0.1	7.8

\*Elements are expressed in weight %.



# Impacts of Dissimilar Coatings

- Sorption/entrainment of Cu or Pb
- Continues exposure after LSLs removed
- Degrades performance of phosphate inhibitors
- Prone to particulate Pb/Cu release
- Must understand treatment change impacts on coatings, as well as Pb and Cu
- Cannot predict optimization or effectiveness of phosphate addition from theory, *but can pilot test with exhumed pipes*
- Cannot form pure stable  $\text{PbO}_2$  layer
- **To control lead release, you must control Fe corrosion/deposition, finished water Mn, DBP precursors, coagulant carry-over, etc.**

# Copper





## Major Factors in Cu Release

- ORP/persistence of oxidants
- pH/Alkalinity/DIC = solubility
- Aging (several variables): Scales recrystallize by themselves, to less soluble forms over years to decades
- [*Ortho*]phosphate, if absolutely necessary, must be above threshold amount related to alkalinity, or it impedes aging process.
- Stagnation time (behavior differs from Pb)
- Flow regime/surface area to volume ratio of real pipe installations affects rate of aging and stagnation release, so coupon-like simulations are often inaccurate





## Current LCR Cu Sampling

- Chemistry and mechanisms of Pb and Cu release have major differences
- **Newest** Tier 1 LCR sites are **25** years old and *get older every monitoring round*, exactly the opposite of copper release risk
- If a site has an LSL, copper *may be sampled from galvanized plumbing*
- States may deem “optimized” even if people have copper levels above the AL, for which there is no public notification
- Technically, there is *no requirement* to report Cu results to residents
- Systems often have zones with different water quality: water quality where Tier 1 Pb sites exist may be considerably different than where high copper levels exist
- Site targeting does not try to capture aggressive waters.

# Lead Treatment Summary





# New Research View of Optimal Corrosion Control Treatment

- OCCT includes *both pure corrosion and control of metal release* (what causes unhealthy exposures)
- OCCT is *much more complicated* than simply adjusting pH or adding phosphate.
- Both soluble and some particulate Pb release can be controlled by treatment
- Surface deposition plays important but unquantifiable role in Pb release
- Metal solubility is still an important factor
  - Varies by factor of 5 to 10 or more across systems
  - Can minimize consumer's chronic/background exposure to metals because soluble release is readily preventable
  - The nature of pipe scales reflecting past treatment history dictates the direction and level of success of lead control approaches

## Essential Tool for Simultaneous Compliance

- Requires addressing all direct and indirect factors causing metal release from the plant through the distribution system.
- Requires treating and solving source of conflict, rather than Band-Aid on symptoms, e.g.
  - DBP precursor removal vs. chloramination
  - Iron/Manganese removal vs. sequestration
  - Operational issues, such as waste discharge constraints resulting in too many IX regeneration cycles
- Anticipate and plan for secondary impacts or synergisms of process additions or changes



## Questions?

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## OCCT/Lead Control Pilot Studies

- PWS must conduct a proper study to look at what is going on in their pipes for their specific water quality zones in DS
- Optimize under the current operating conditions
- New studies needed well in advance of future treatment or operational changes that could impact lead or copper release. May take years.
- New studies needed to anticipate other DS metal or radionuclide release side effects of changes
- This is *SAME concept* as use of jar tests for coagulation, column tests for filter media evaluation, column tests for As removal, pilot tests for ozonation or UV, etc.

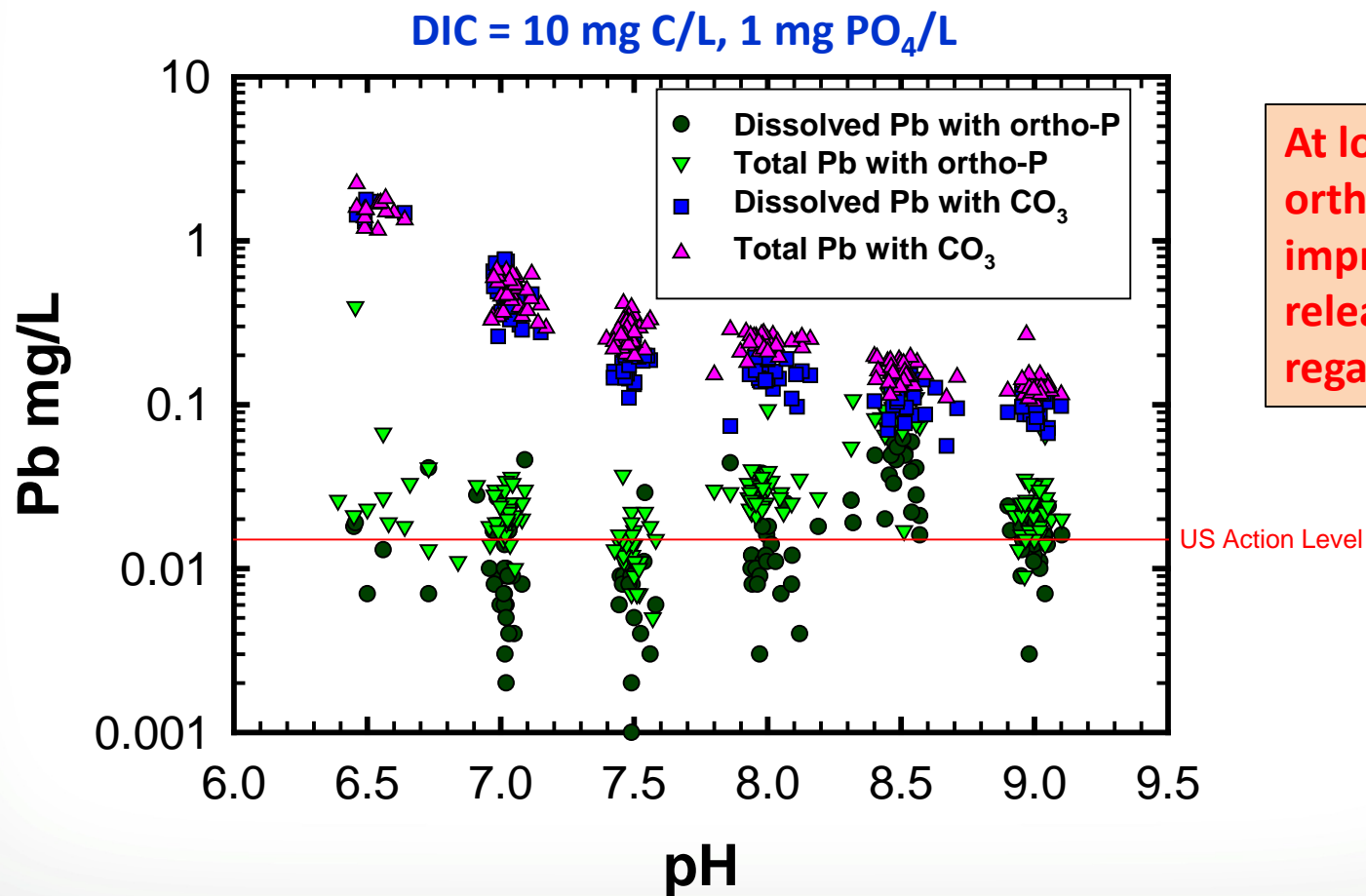


## Simultaneous Compliance IS Possible

- Recognition of diverse DS WQ relationships
- Recognition of DS and premise plumbing materials
- Commitment to address sources of chemical conflicts, e.g.
  - Removal of interfering substances to metal release
  - DBP precursors
  - Lead sources (notably LSLs)
- Holistic design and integration of processes
- Homogenization of WQ across zones in system to extent possible
- Resources to take actions necessary for O&M of plants and DS
- Necessity of pilot studies to tailor to conditions



# Effect of pH and $\text{PO}_4$ on Pb Release



**At low DIC,  
orthophosphate  
improves lead  
release  
regardless of pH**