Understanding the Impact of Changes in Water Chemistry on Concentrations of Lead in Drinking Water

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Hong Kong Institution of Engineers – Environmental Division

Acknowledgments

- Yeunook Bae, Anna Ivarson, Lia Schattner, Violla Liu, Weiyi Pan, Anushka Mishra, and Chao Pan
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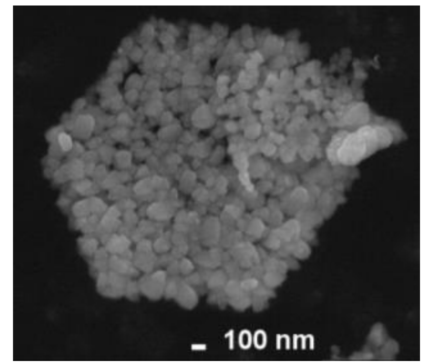
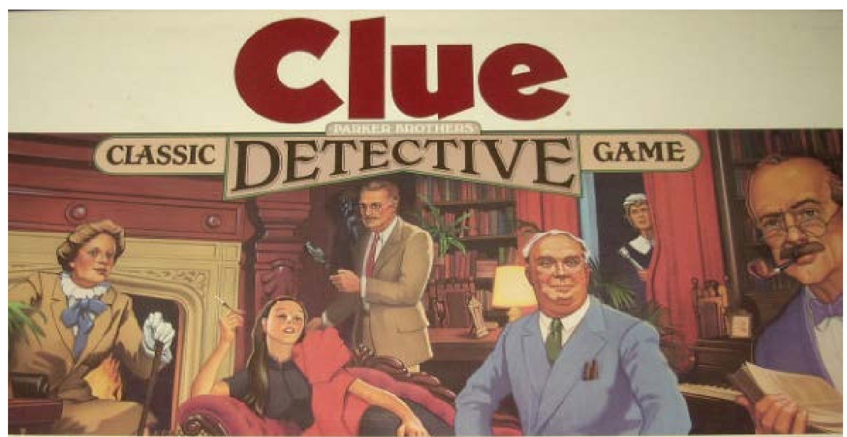
- Greg Welter (O'Brien and Gere Engineers)
- DC Water and Providence Water



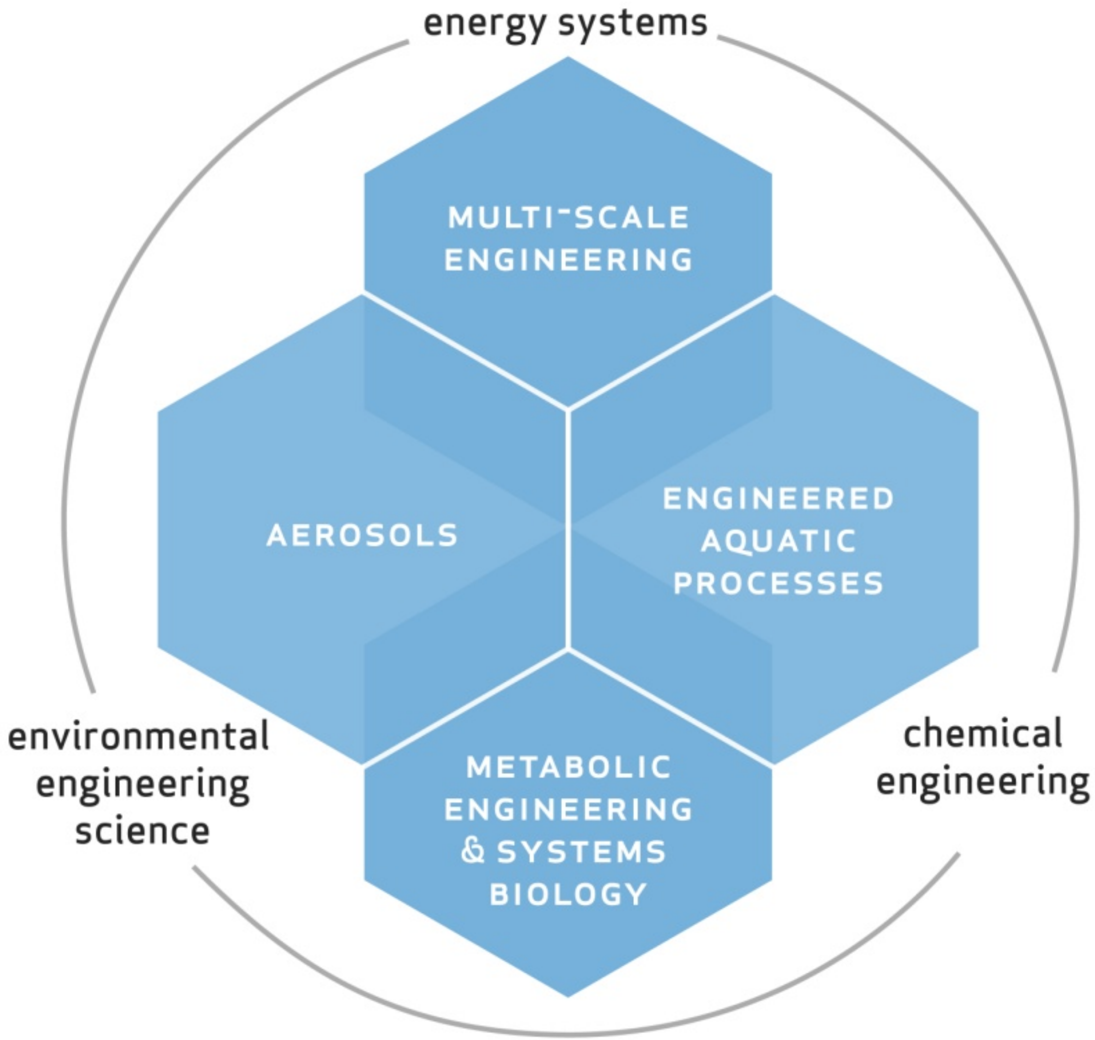



Water Resource Regions
Not Here
(Washington State)
Souris Red
Rainy
Great Lakes
New
England
Missouri
Upper
Mississippi
Mid
Atlantic
Upper
Colorado
California
St. Louis
Not Here
(Washington, DC)
Lower
Colorado
Rio
Grande
Texas
Hawaii
Alaska
Carribean

Washington University in St. Louis

- Founded in 1853
- A private research university
- 14,000 students, about half graduate and half undergraduate
- Undergraduate program ranked 19th in the U.S., Medical School ranked 4th, School of Social Work ranked 1st
- Undergraduate admissions requirements equal to those of Stanford and MIT
- 24 Nobel Laureates

Energy, Environmental and Chemical Engineering



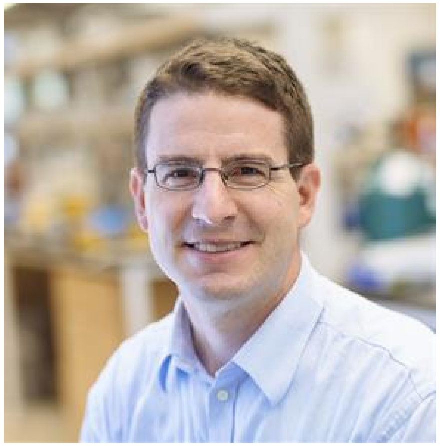
- 19 faculty
- 85 Ph.D. students
- 114 undergraduates
- 35 masters students

Engineered Aquatic Processes

John Fortner

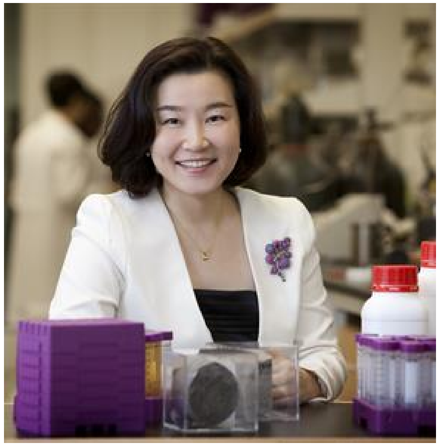
environmental applications and implications of nanomaterials

Daniel Giammar



aquatic chemistry, water treatment, environmental remediation

Young-Shin Jun



environmental nanochemistry, carbon sequestration, water treatment

Kimberly Parker

Fangqiong Ling

Microbiome of the built environment, genomics, machine learning, theory

environmental organic chemistry, photochemistry, water treatment

Aquatic Chemistry Laboratory

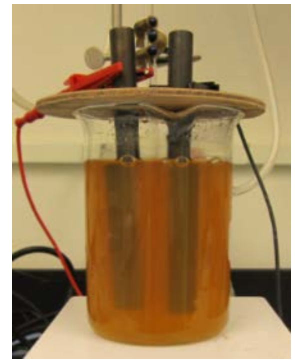
Investigate reactions affecting the fate and transport of heavy metals, radionuclides, and other inorganic contaminants in natural and engineered aquatic systems.

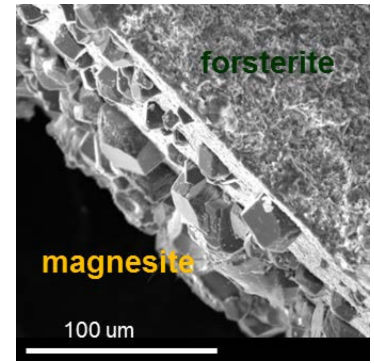
Research Techniques

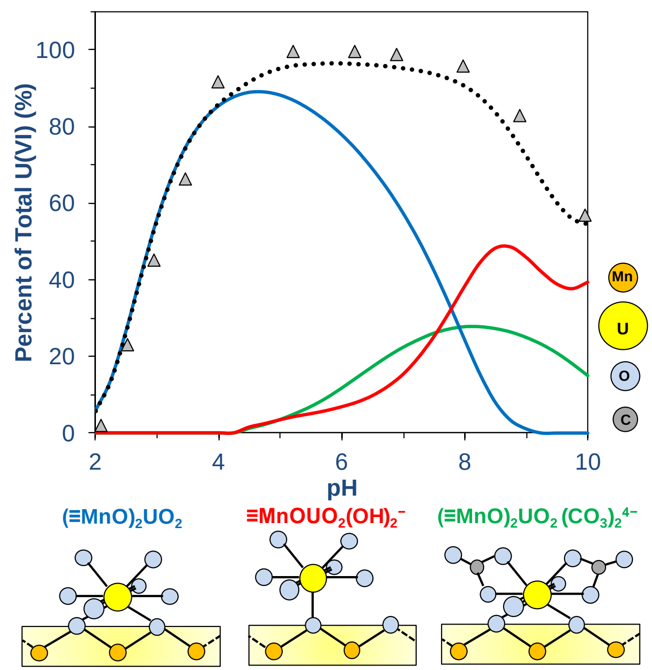
- Aquatic Chemistry
- Solid Phase Characterization
- Modeling

Research Areas

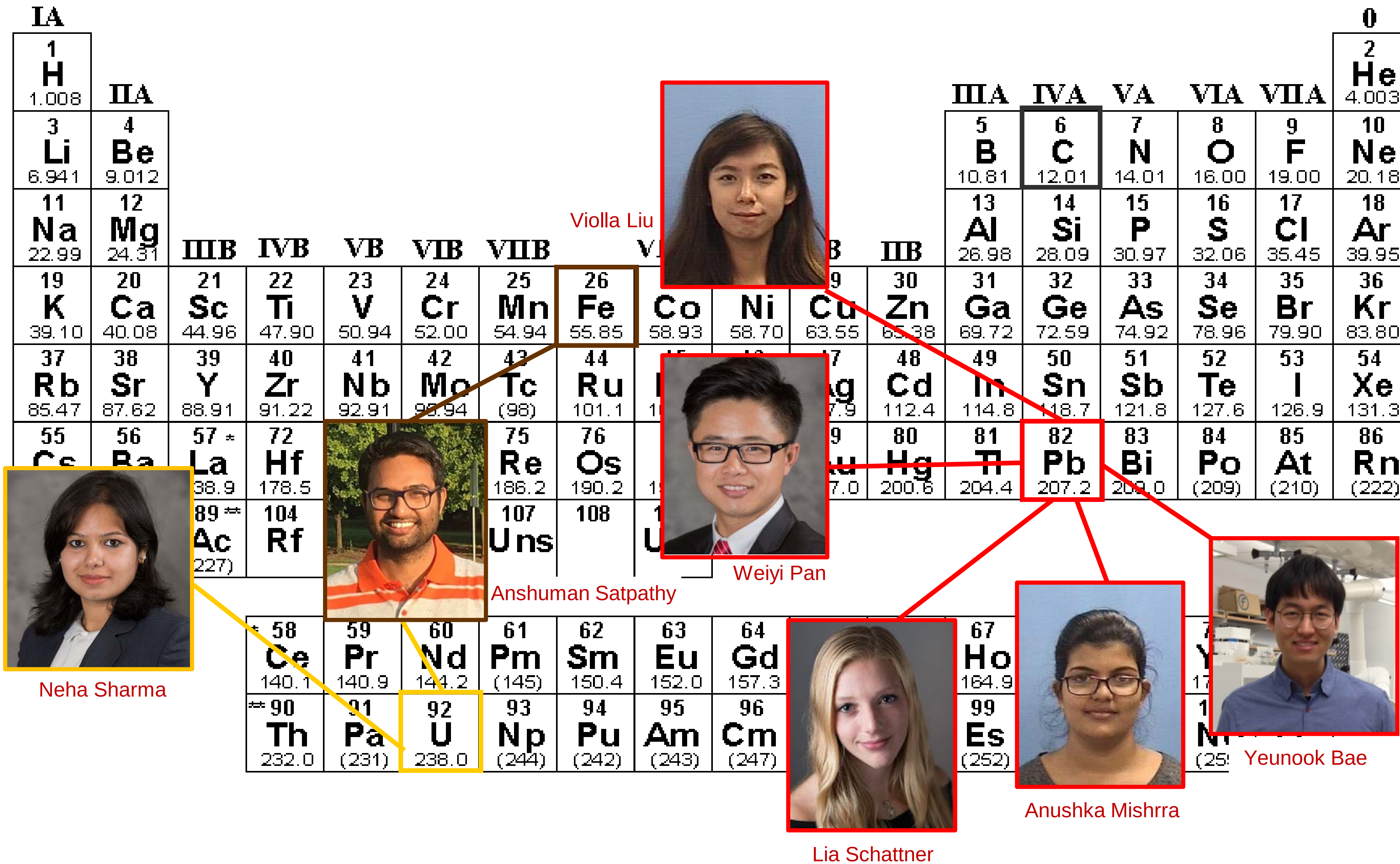
- Drinking Water Supply and Treatment
- Biogeochemical Processes in Soil and Groundwater
- Environmental Impacts of Fossil Energy Byproducts







Aquatic Chemistry Lab Fall 2018



Mobility of Metals in Soil and Groundwater

Redox-Driven Recrystallization of PbO_2 and UO_2

Trace Metal Dynamics and Limitations in Wetlands

Drinking Water Supply and Treatment

Phosphate for Lead Corrosion Control

Silicates for for Lead Corrosion Control

Uranium Adsorption to Nanoparticles and Electrocoagulation

Environmental Impacts of Fossil Energy Byproducts

Carbon Sequestration in Fractured Basalts

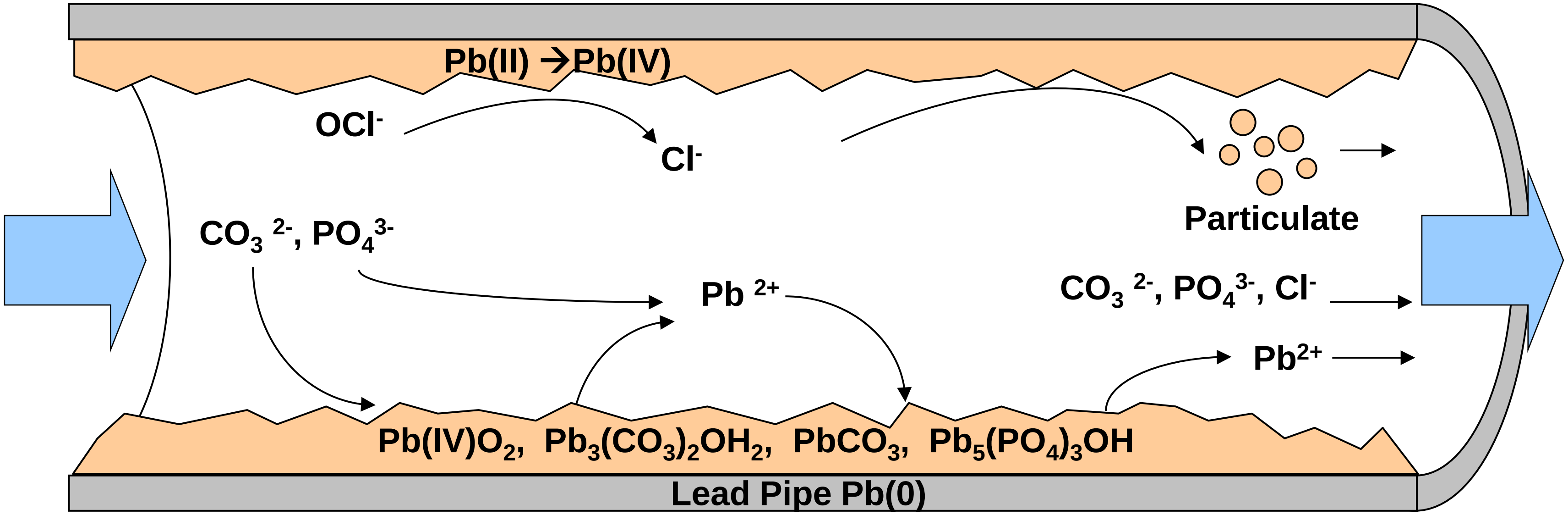
Radical Oxidants in Hydraulic Fracturing

Lead in Drinking Water

- Historical use of lead (plumbing = Pb) for conveying and storing water.
- Widespread use starting in the late 19th century to connect residences to water mains.
- Use dropped off in 1930, but not prohibited until 1986.
- Estimate of 7-10 million lead service lines in the United States.
- U.S. Lead and Copper Rule in 1991 set an action level of 15 µg/L.
  - 90th percentile of homes samples must be below the action level.
  - If not, then must implement corrosion control.
  - Current revisions underway.

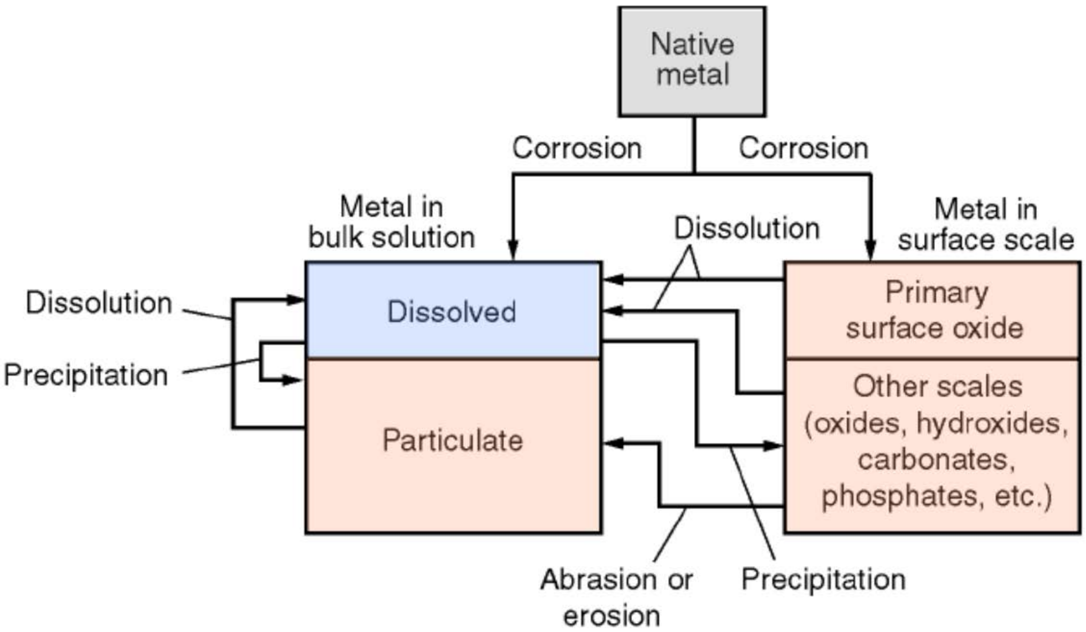
Roman pipes in Bath, England
Source: wikipedia

Lead Phases in Lead Service Lines

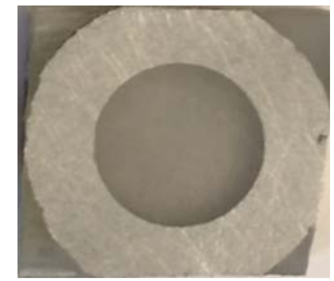


- Lead(IV) oxide (PbO_2) and lead phosphate solids are the least soluble.
- Lead carbonate and hydroxycarbonate can have solubility minimized by controlling pH and alkalinity.
- Changes in distribution system water chemistry can destabilize corrosion products in premise plumbing.

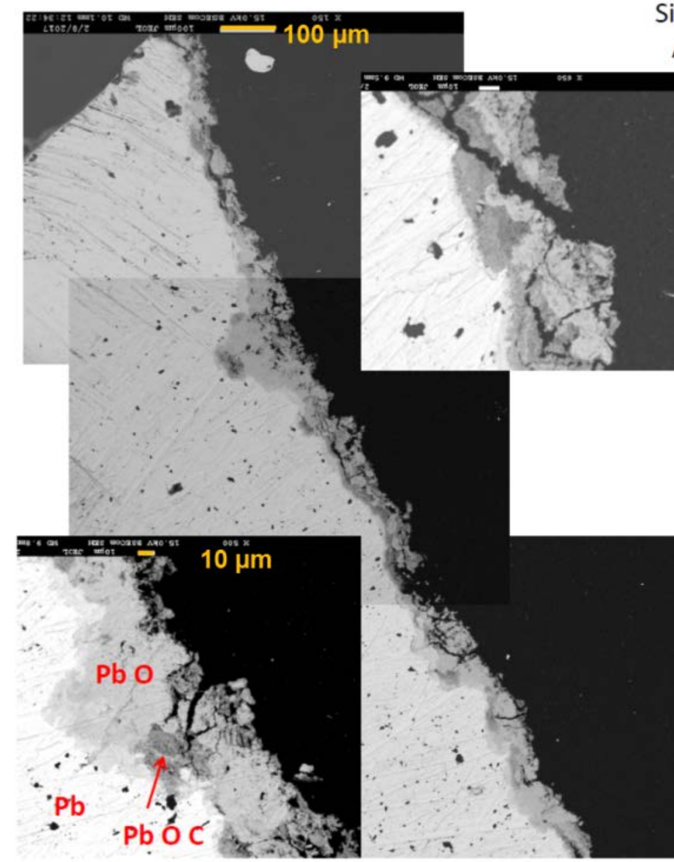
Formation of Scales in Lead Pipes



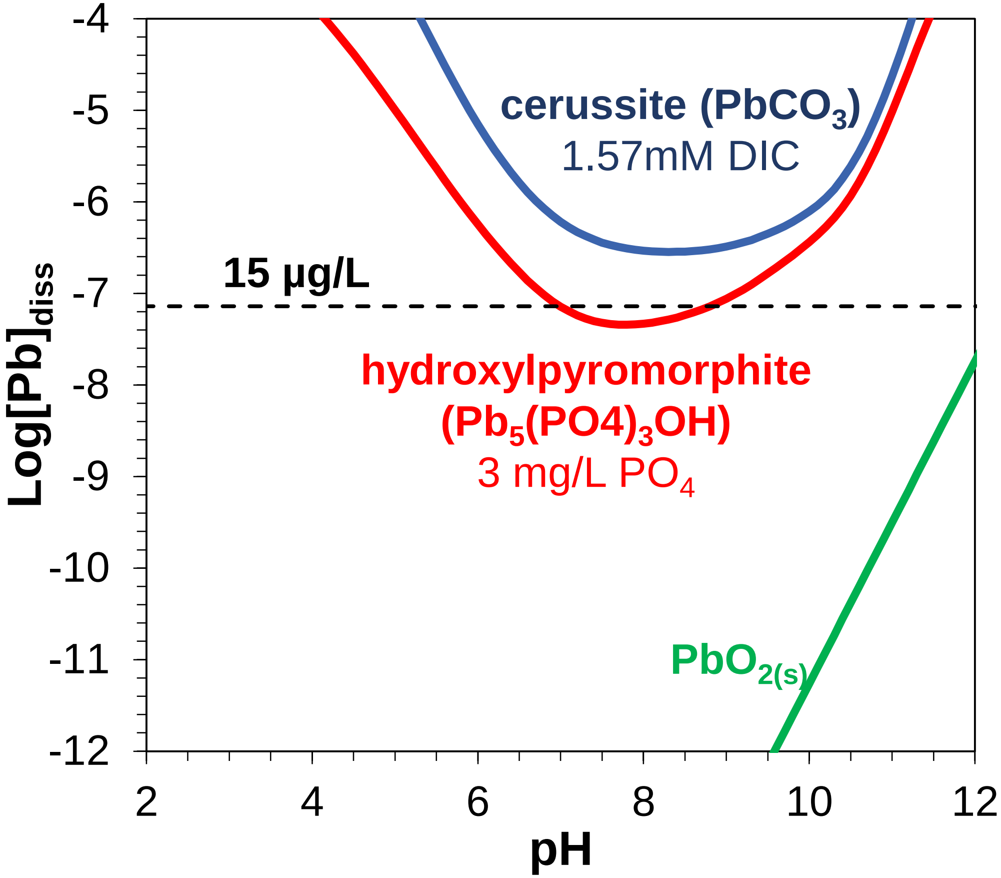
Source: MWH, 2005, *Water Treatment Principles and Design*



Side A



Equilibrium Lead Concentrations



Lead concentrations influenced by:

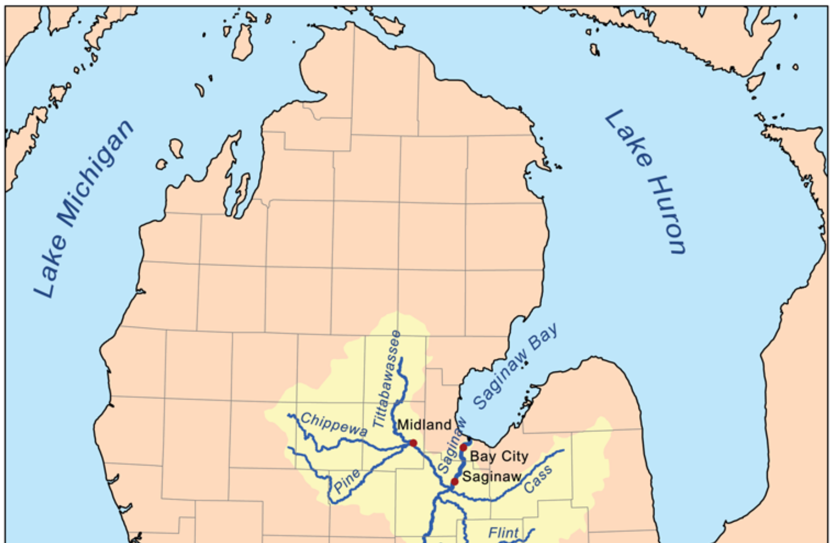
- pH
- Dissolved inorganic carbon (DIC)
- Disinfectant
- Orthophosphate
- Natural organic matter (NOM)

Outline

- Overview of Lead in Tap Water
- **Flint Water Crisis – Interrupted Corrosion Control**
- DC Water Crisis - Response to a Change in Disinfectant
- Providence – Use of Phosphate for a High pH System
- Conclusions

Flint Water Crisis - Timeline

1883-1967	Flint treats Flint River as its drinking water source.
1967-2014	Flint purchases water from Detroit (Lake Huron is the source).
Mid-1990's	Detroit begins adding orthophosphate (PO_4^{3-}) for corrosion control.
2013	Flint emergency city manager signs agreement to join Karegnondi Regional Water Authority, but pipeline not available until 2017.



it River as its source. It does not implement
ontrol.

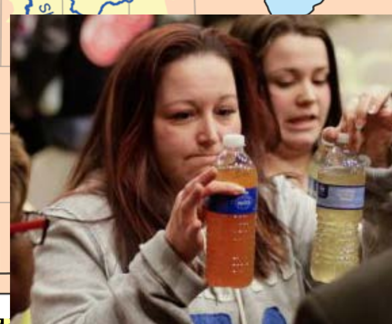
egin almost immediately.

nethanes (disinfection byproduct).

ers) contacts EPA regarding high lead.

releases results showing elevated lead.

presents findings on increased incidence of
ildren following the switch of water source.



placement of lead and
aucet filter
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s/wp-
monitor.
ginawrivermap.png

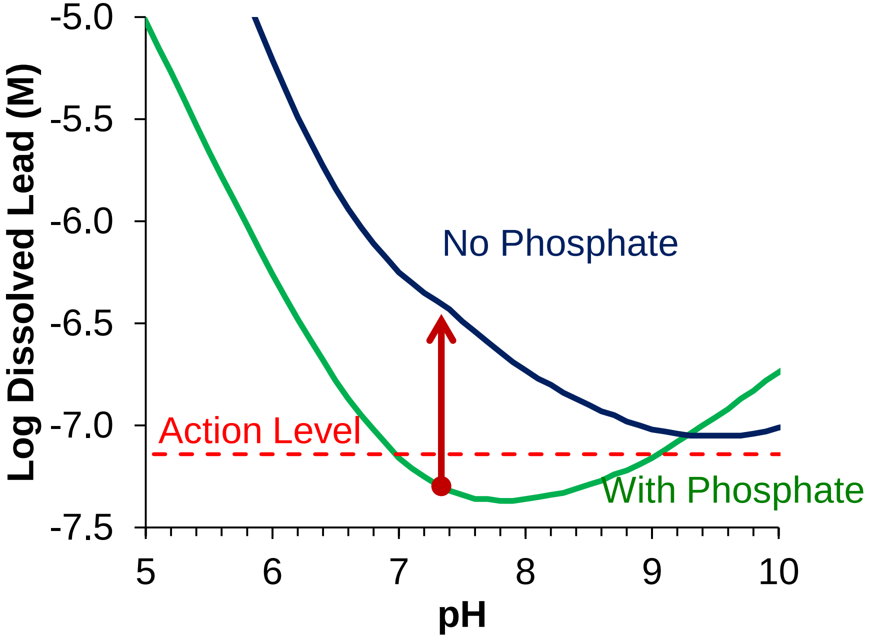
news.yahoo.com

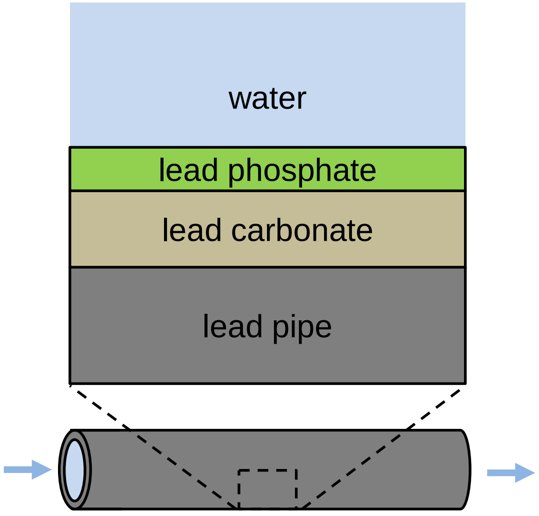
vtnews.vt.edu

Disclosure: Daniel Giammar wa... ...
Concerned Pastors for Social Action v. Khouri

Flint Water Crisis – Water Chemistry

While there are differences in the compositions of the Flint River and Lake Huron water, the biggest difference was the lack of added phosphate to the Flint River water.





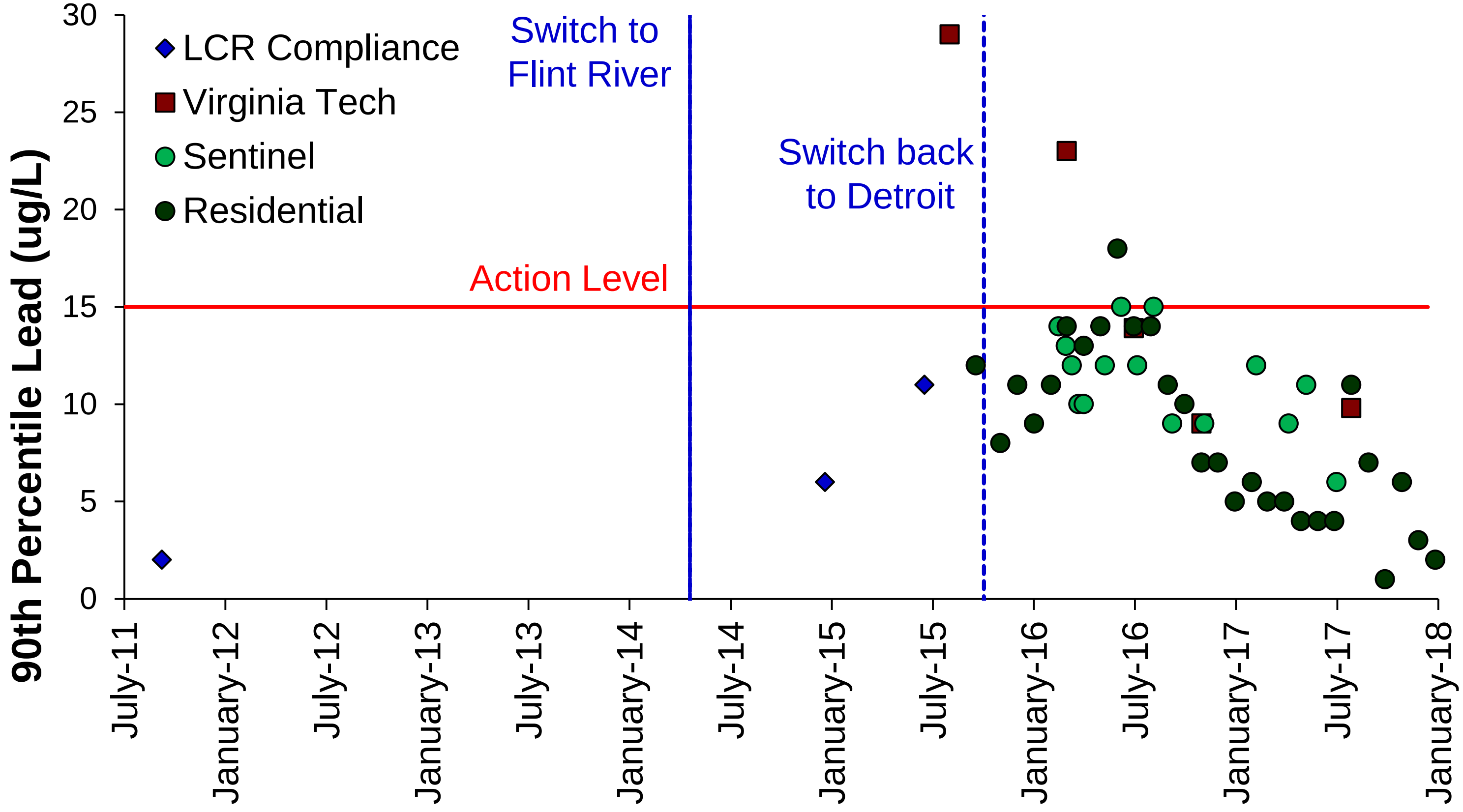
Did I they really need a Ph.D. environmental engineer for this quote?

"In going from having a corrosion inhibitor to not having one, you might have expected to have increased corrosion."

New York Times, January 23, 2016

Flint Water Crisis – Tap Water Lead

- Switch of water source without orthophosphate addition.
- Increased lead releases were apparent after switch and before outside attention.



Compliance monitoring data available at www.cityofflint.com; most recent only available in Flint Water Advisory Task Force Report.
Sentinel Site (~600 locations) and Extended Sentinel Site (~160 locations) and Residential data (>320,000 samples) available at http://www.michigan.gov/flintwater.
Virginia Tech data available at http://flintwaterstudy.org/.

Outline

- Overview of Lead in Tap Water
- Flint Water Crisis – Interrupted Corrosion Control
- **DC Water Crisis - Response to a Change in Disinfectant**
- Providence – Use of Phosphate for a High pH System
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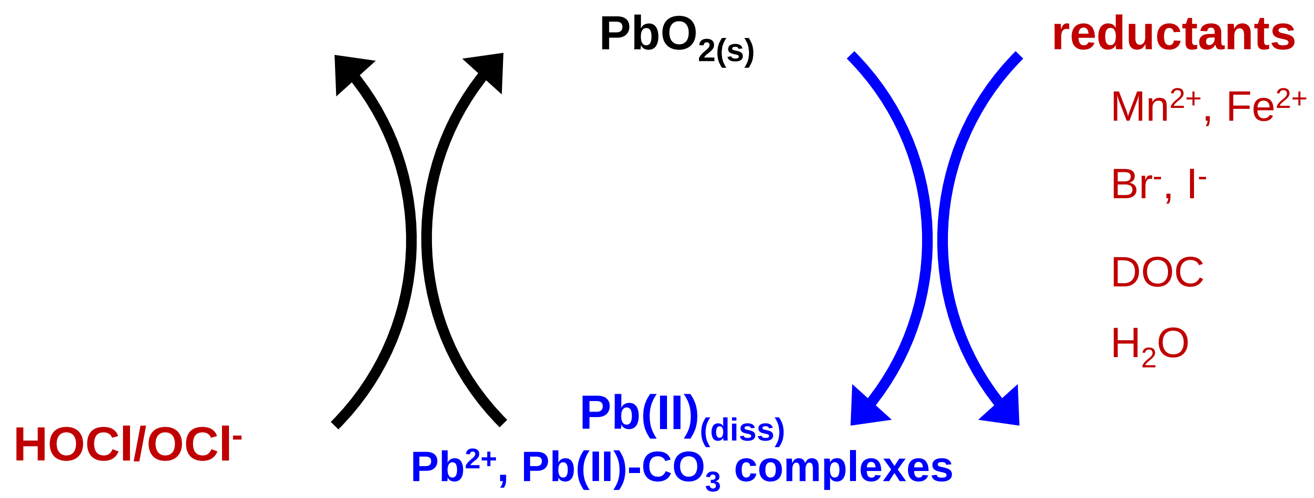
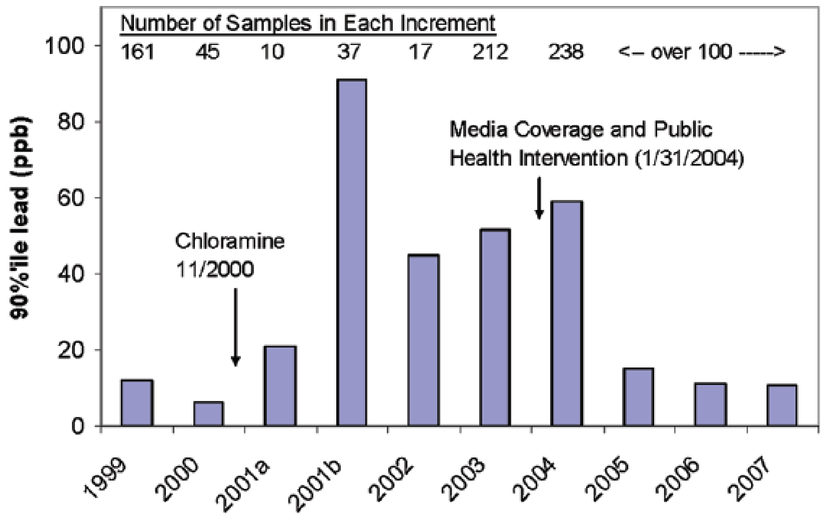
Formation and Dissolution of PbO_2

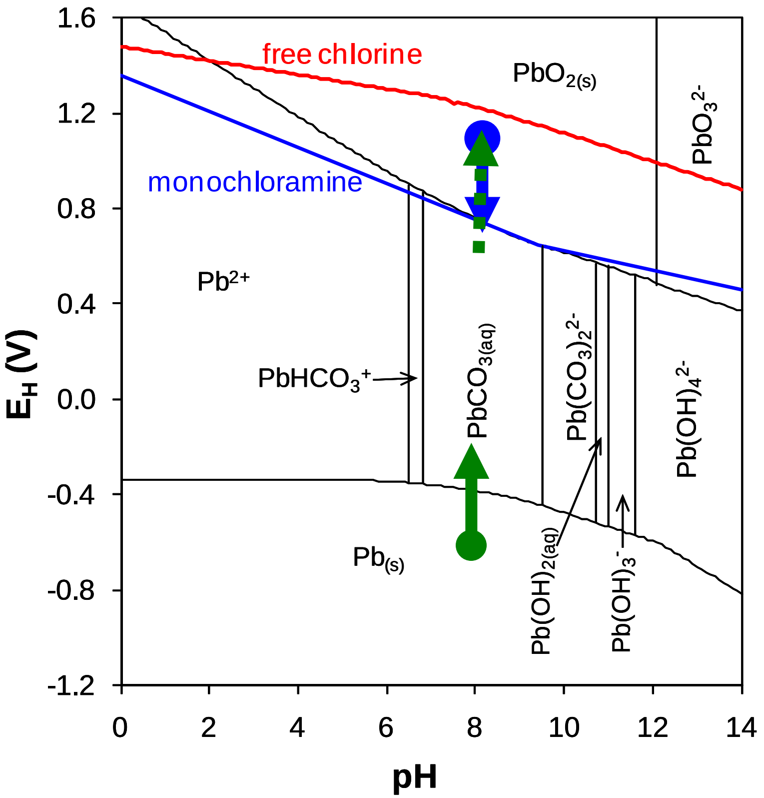


- PbO_2 can only be formed in the presence of free chlorine.
- When free chlorine is depleted, PbO_2 dissolves and releases lead to the water.
- Switching from free chlorine to chloramine (e.g., for control of disinfection byproducts) can result in lead release from PbO_2.
- Presence of reductants, including dissolved organic carbon, enhances the dissolution of PbO_2.

Lead in Washington, DC Drinking Water

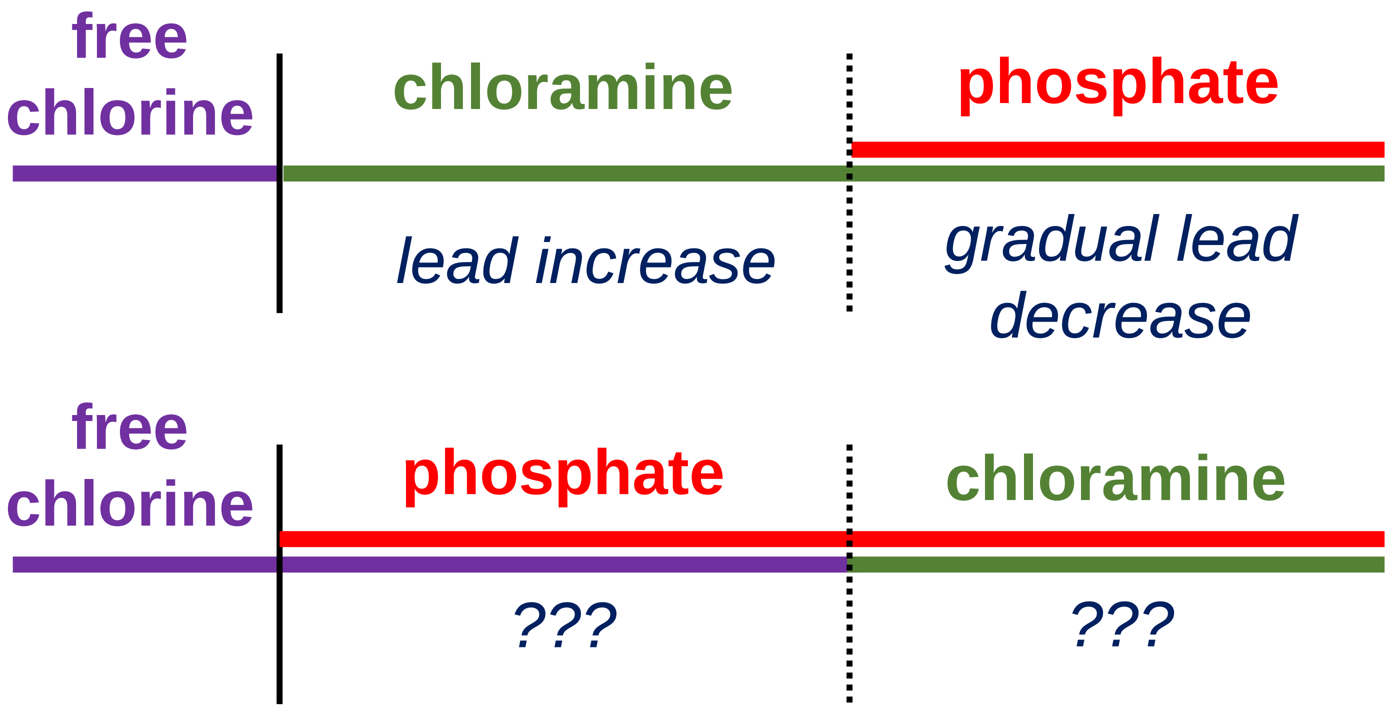


Source: Edwards et al., 2009, *Environ. Sci. Technol.*



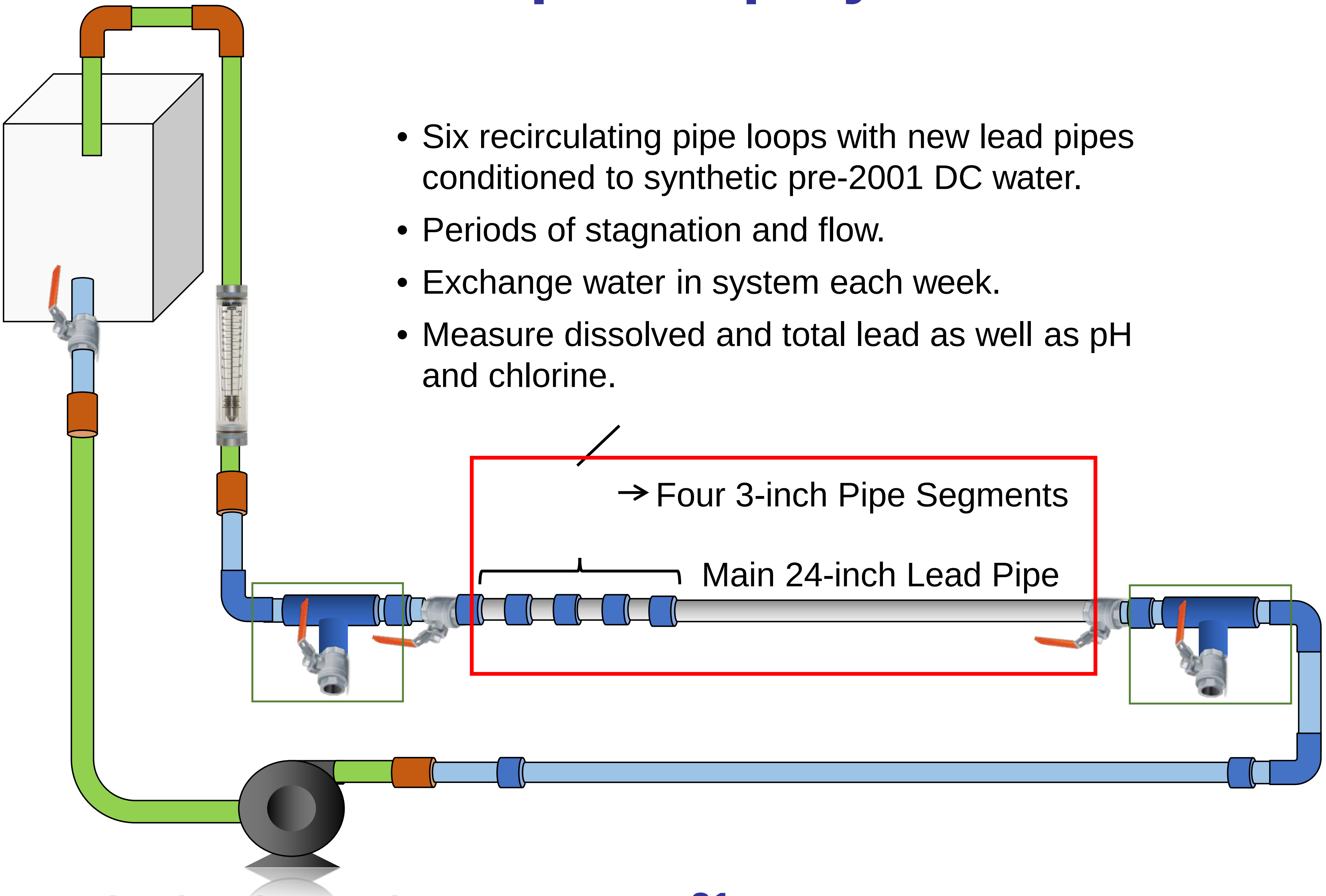
- Disinfectant switched from free chlorine to chloramine for secondary disinfection to reduce concentration of chlorinated disinfection byproducts.
- Switch resulted in breakdown of PbO_2 and release of lead to solution.
- Controlled by addition of orthophosphate and adjustment of pH.

Can phosphate addition minimize lead release when the disinfectant is switched?



Lead Pipe Loop System

- Six recirculating pipe loops with new lead pipes conditioned to synthetic pre-2001 DC water.
- Periods of stagnation and flow.
- Exchange water in system each week.
- Measure dissolved and total lead as well as pH and chlorine.

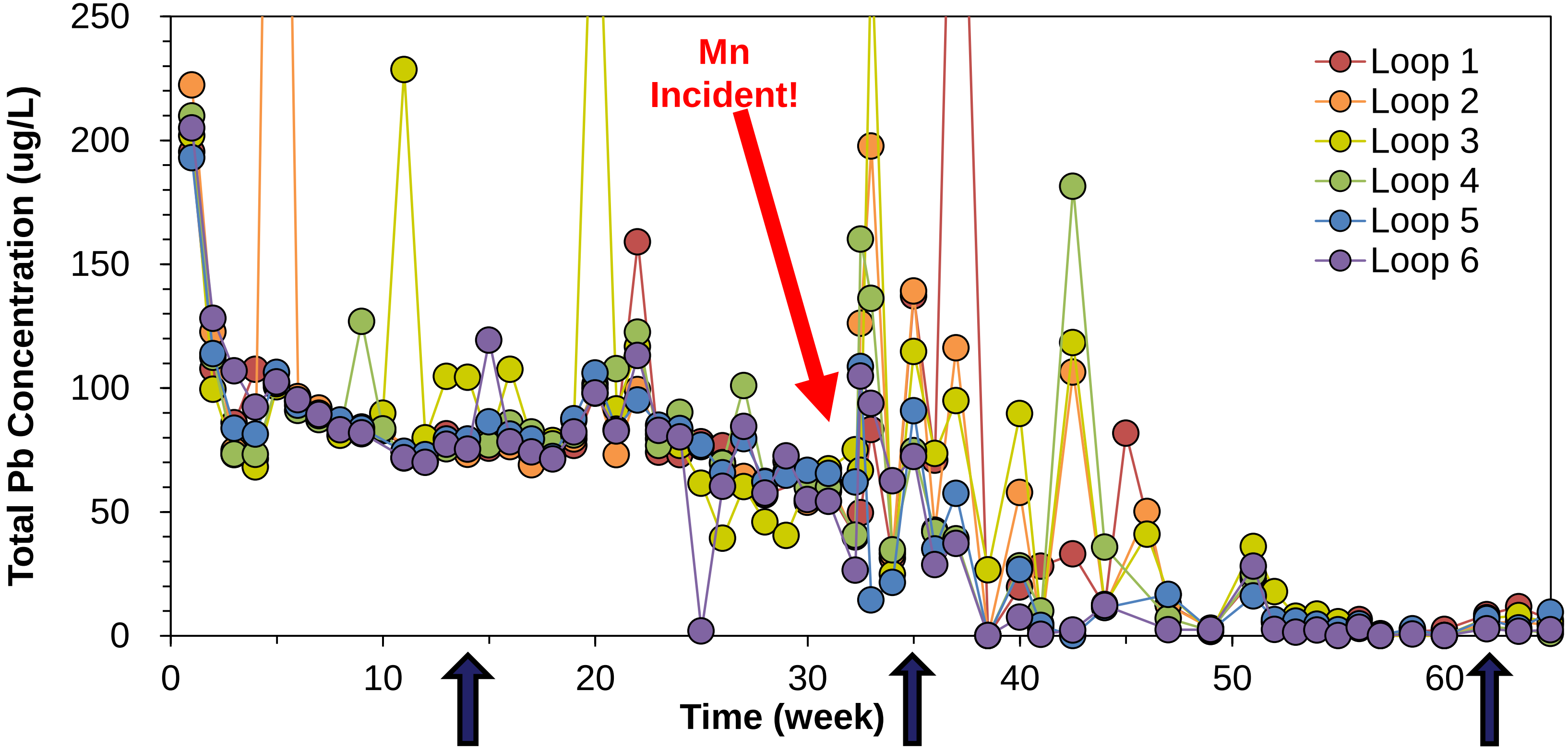


Lead Pipe Loop System

- 6 replicate loops
- Initial pH 7.7
- DIC = 1.57 mM (19 mg/L C)
- Initial Cl_2 conc. = 1-2 mg/L.

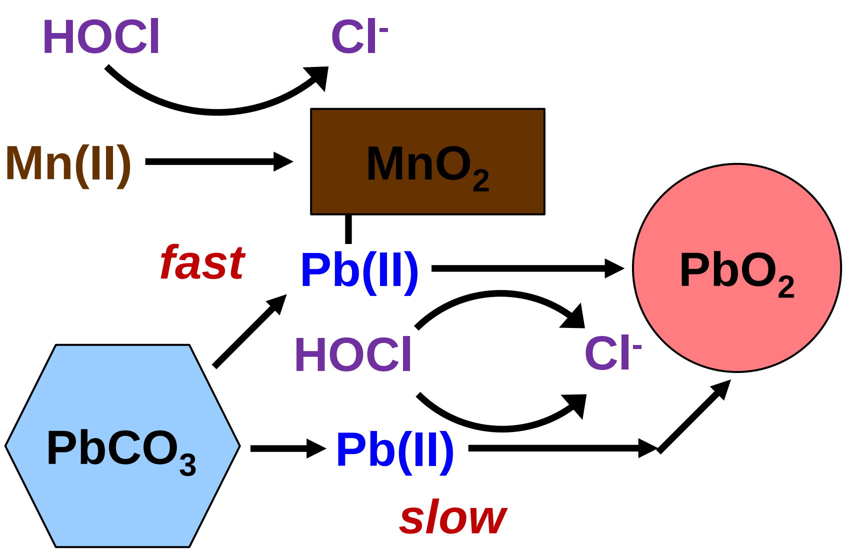
- Exchange with the fresh synthetic tap water every week (168 hr).
- Daily, 8 hour stagnation and 16 hour recirculation.
- Measure Cl_2 concentration and readjust to initial level (daily).
- Measure Pb concentration (8 hr and 168 hr samples) and pH (daily).

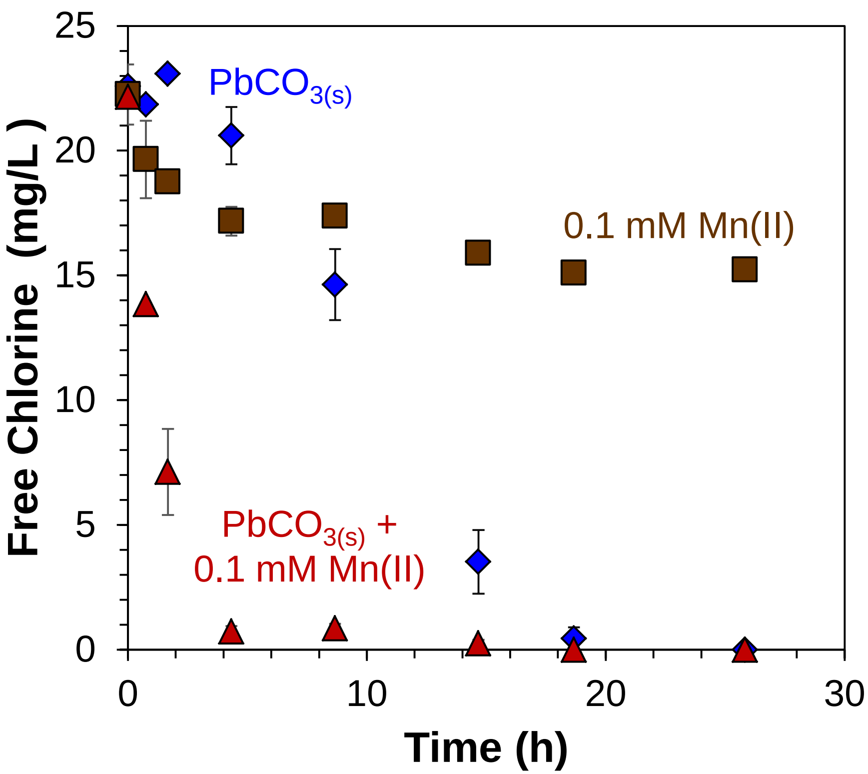
Conditioning Lead Pipes with pre-2000 DC Water



lead pipe segments collected for scale analysis

“The Mn Incident”

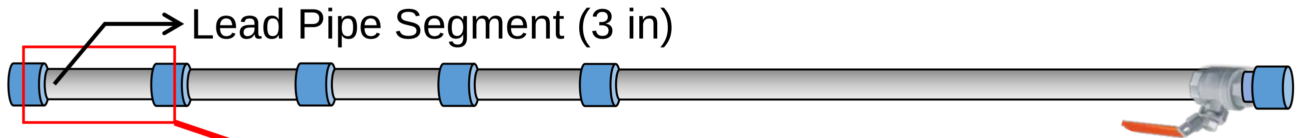




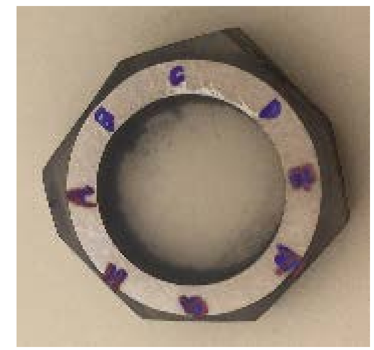
- Formation of Mn oxide allowed fast oxidation of adsorbed Pb(II) to PbO_2.
- The presence or absence of Mn(II) in distribution system water may explain why not all systems with free chlorine have had PbO_2 observed in lead pipe scales.

Scale Analysis

Lead Pipe Parts



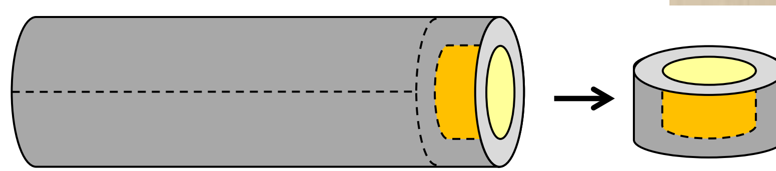
101st day (15th week)



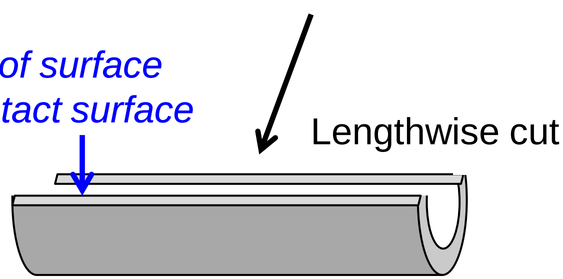
Original pipe segment (3-inches)

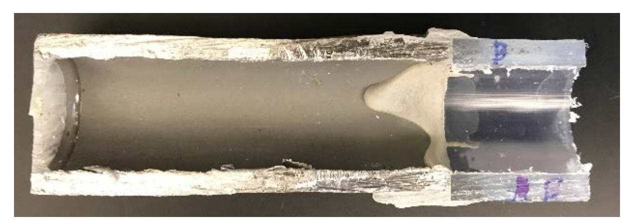
Fill one end partially with epoxy

Cut segment into a disk (0.5-inch thick) and two half cylinders



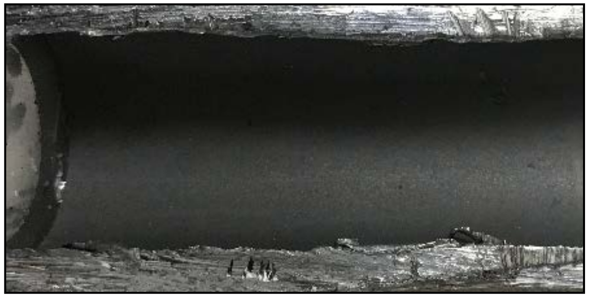
Optical photographs of surface
Raman analysis of intact surface





Scale Analysis

14 weeks



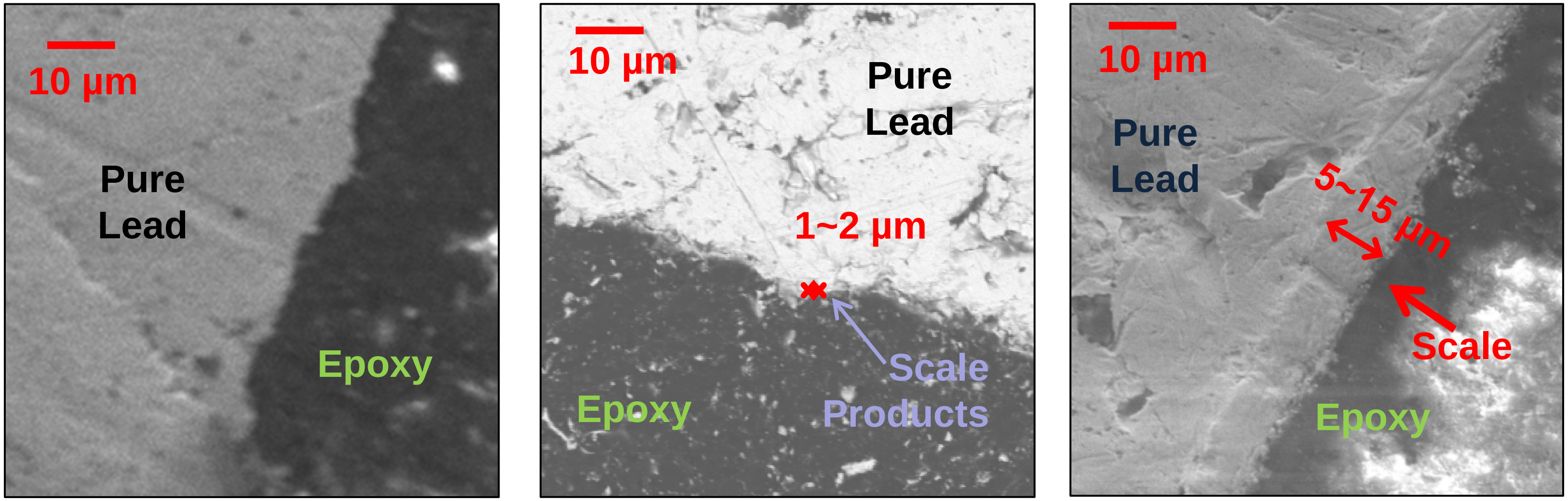
35 weeks

62 weeks

- Scale gradually develops on the pipe surface and ultimately grows to about 15 µm thickness.
- Raman spectroscopy with a microprobe tracks the change in lead-containing phases from lead(II) oxides and carbonates to PbO_2.

Scale Analysis

14 weeks | 35 weeks | 62 weeks



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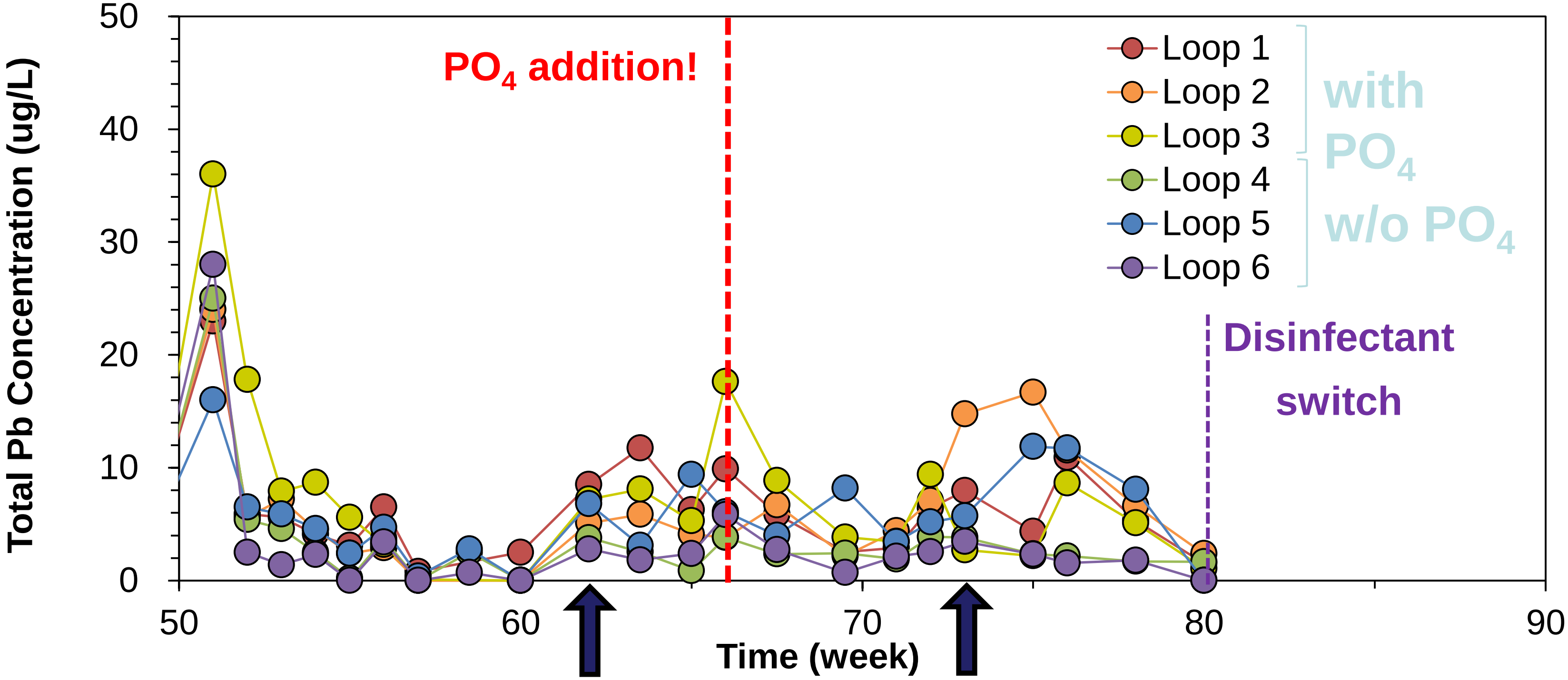
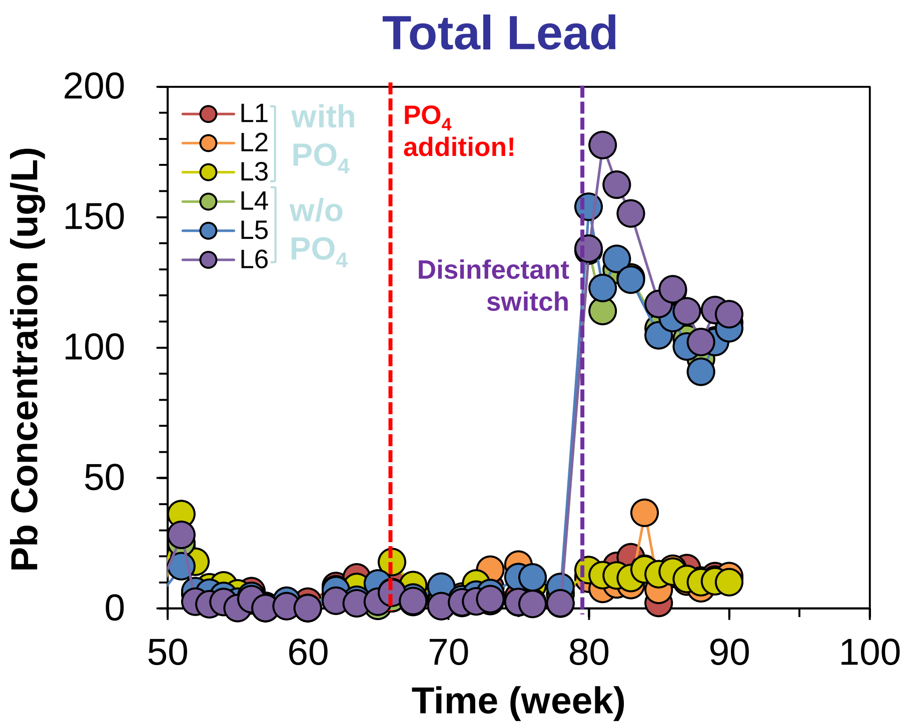
Phosphate Treatment

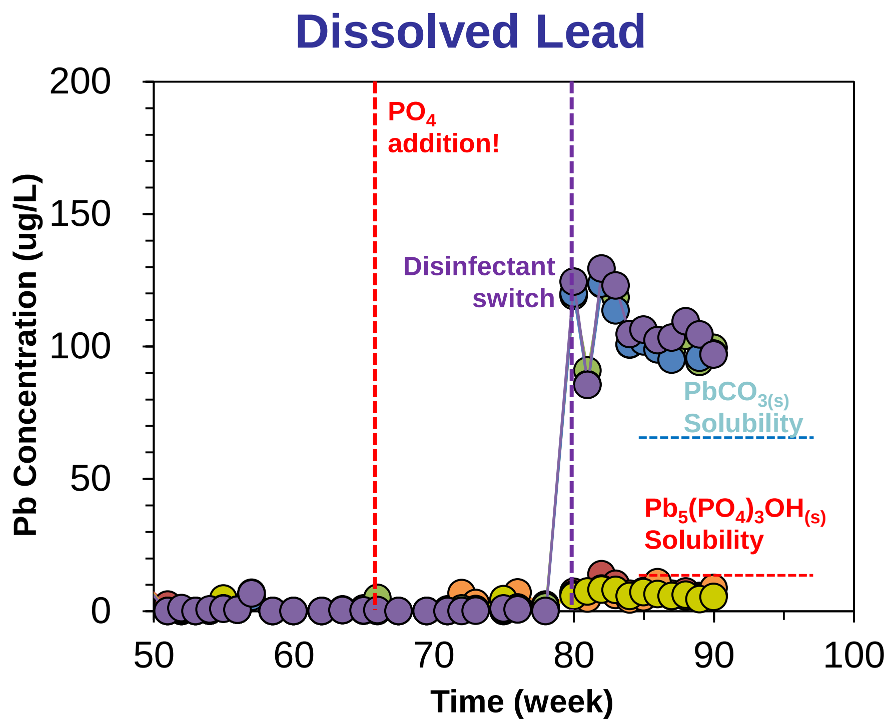


lead pipe segments collected for scale analysis

- No substantial effect of orthophosphate treatment on pipes receiving free chlorine.
- Scale analysis found no significant changes in phase present.

Disinfectant Switch after Phosphate Treatment





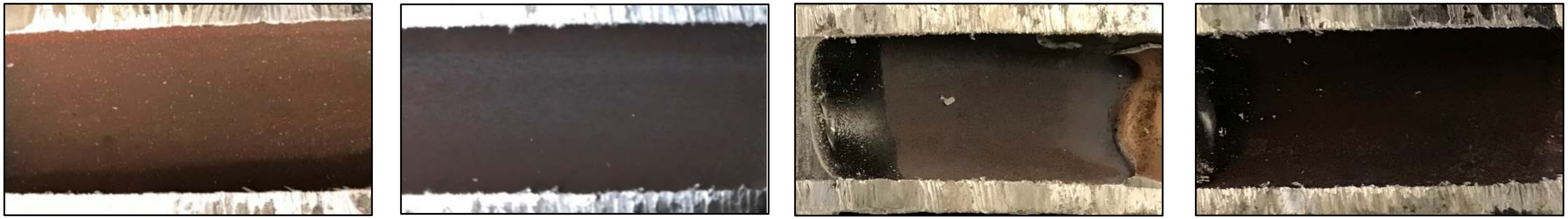
- With PO_4: predicted solubility of hydroxylpyromorphite = 12 µg/L
- Without PO_4: solubility of cerussite = 67 µg/L

Scale Analysis

Conditioning **62 weeks**

Phosphate Pretreatment **73 weeks**

Switch to Chloramine **83 weeks (w PO_4)** **83 weeks (w/o PO_4)**



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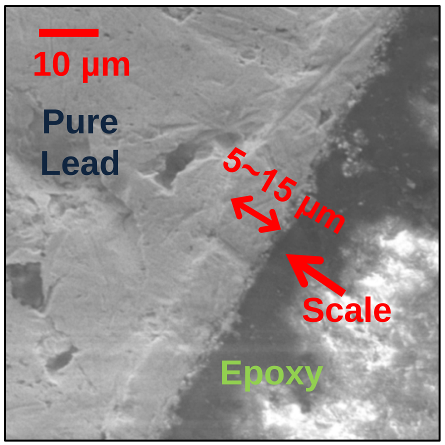
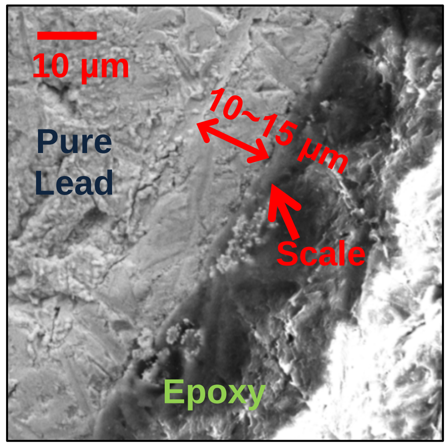
Scale Analysis

Conditioning
62 weeks

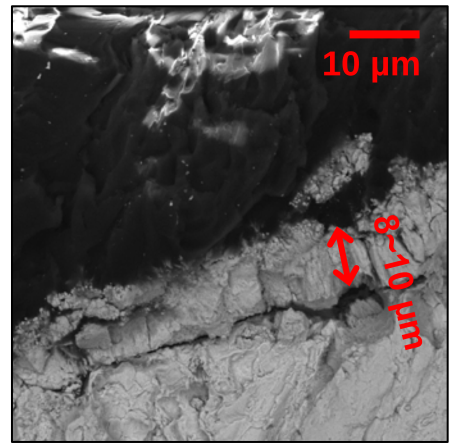


Phosphate Pretreatment
73 weeks

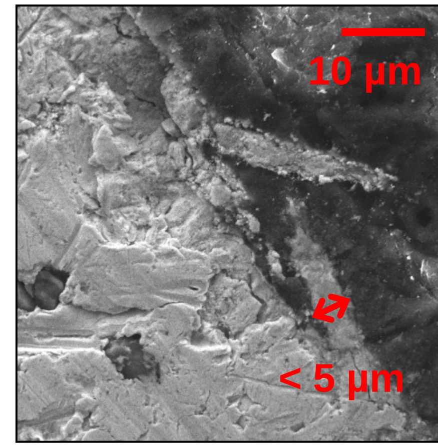


Switch to Chloramine

83 weeks (w PO_4)

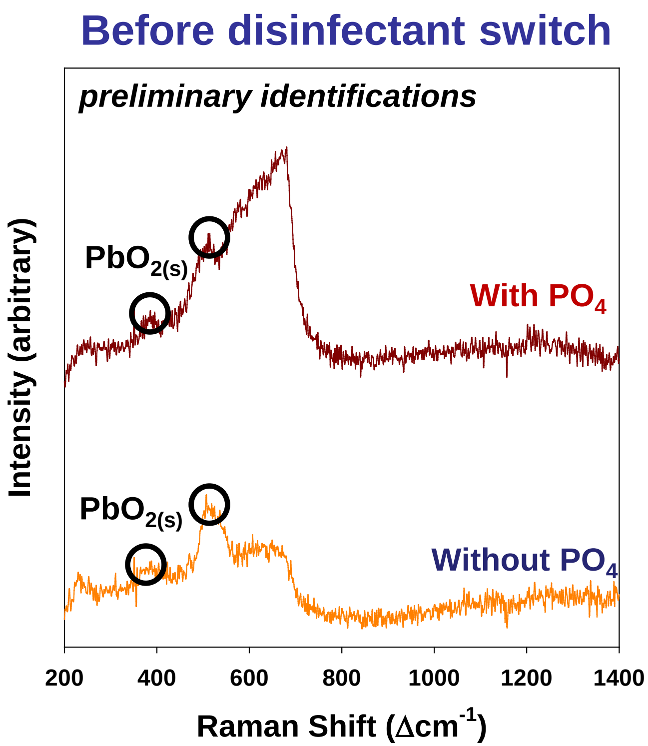


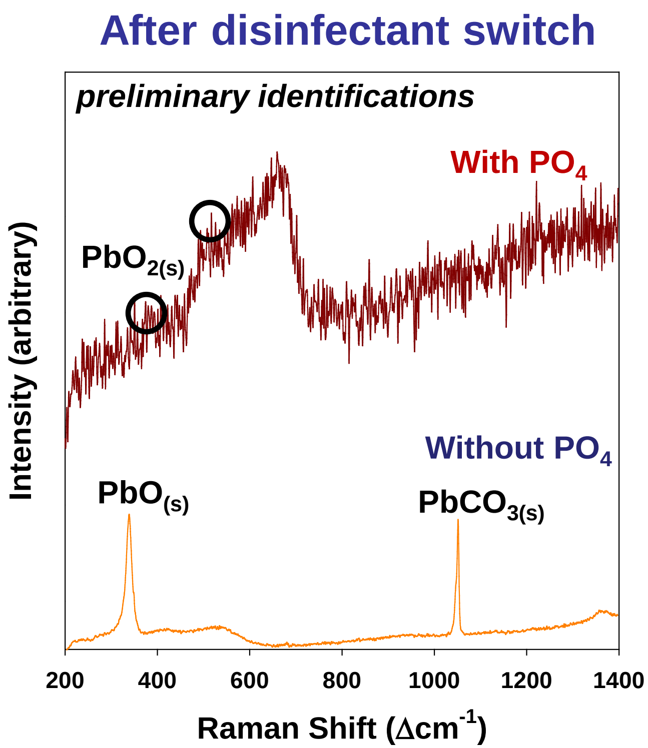
83 weeks (w/o PO_4)



- No obvious changes in scale appearance with phosphate pretreatment while still feeding free chlorine.
- After switch from free chlorine to chloramine:
  - with orthophosphate: scale contains phosphorus but is still dominated by PbO_2.
  - without orthophosphate: scale is thinner, has pits, and an overall different morphology and becomes dominated by Pb(II) oxide and carbonate solids.

Scale Analysis





- Before disinfectant switch, $PbO_{2(s)}$ (plattnerite) present regardless of orthophosphate addition.
- After the switch, plattnerite persisted when orthophosphate present, but lead(II) solids litharge (PbO) and cerussite ($PbCO_3$) observed when orthophosphate was absent.

Key Findings with PbO_2 Scales

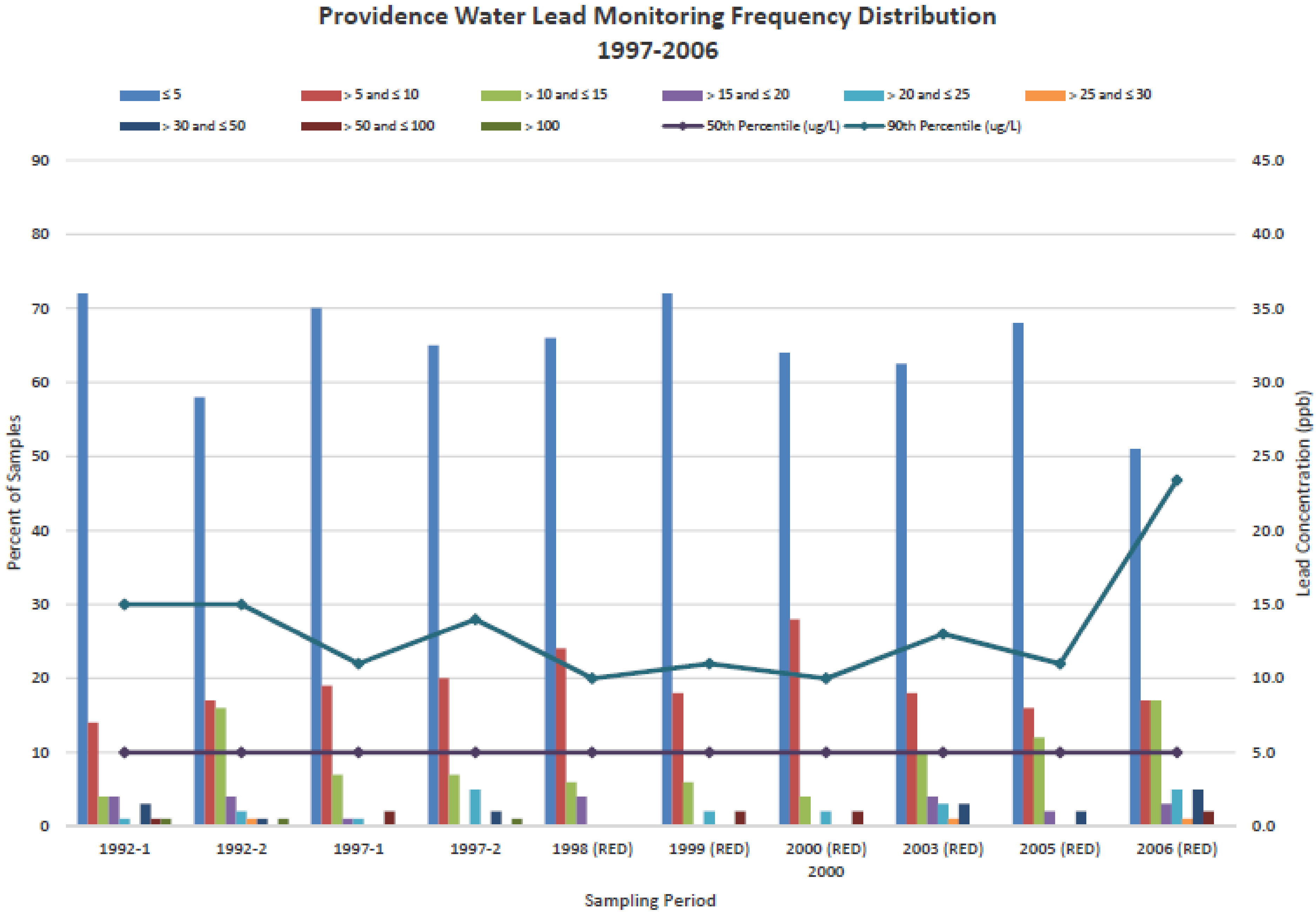
- Scales of PbO_2 develop on the inner surfaces of lead pipes reacted with free chlorine in one year.
- Manganese oxides accelerate PbO_2 formation.
- PbO_2 is unstable in the presence of monochloramine and rapidly breaks down and releases lead to solution.
- Phosphate can substantially mitigate the dramatic lead release associated with a disinfectant switch.

Outline

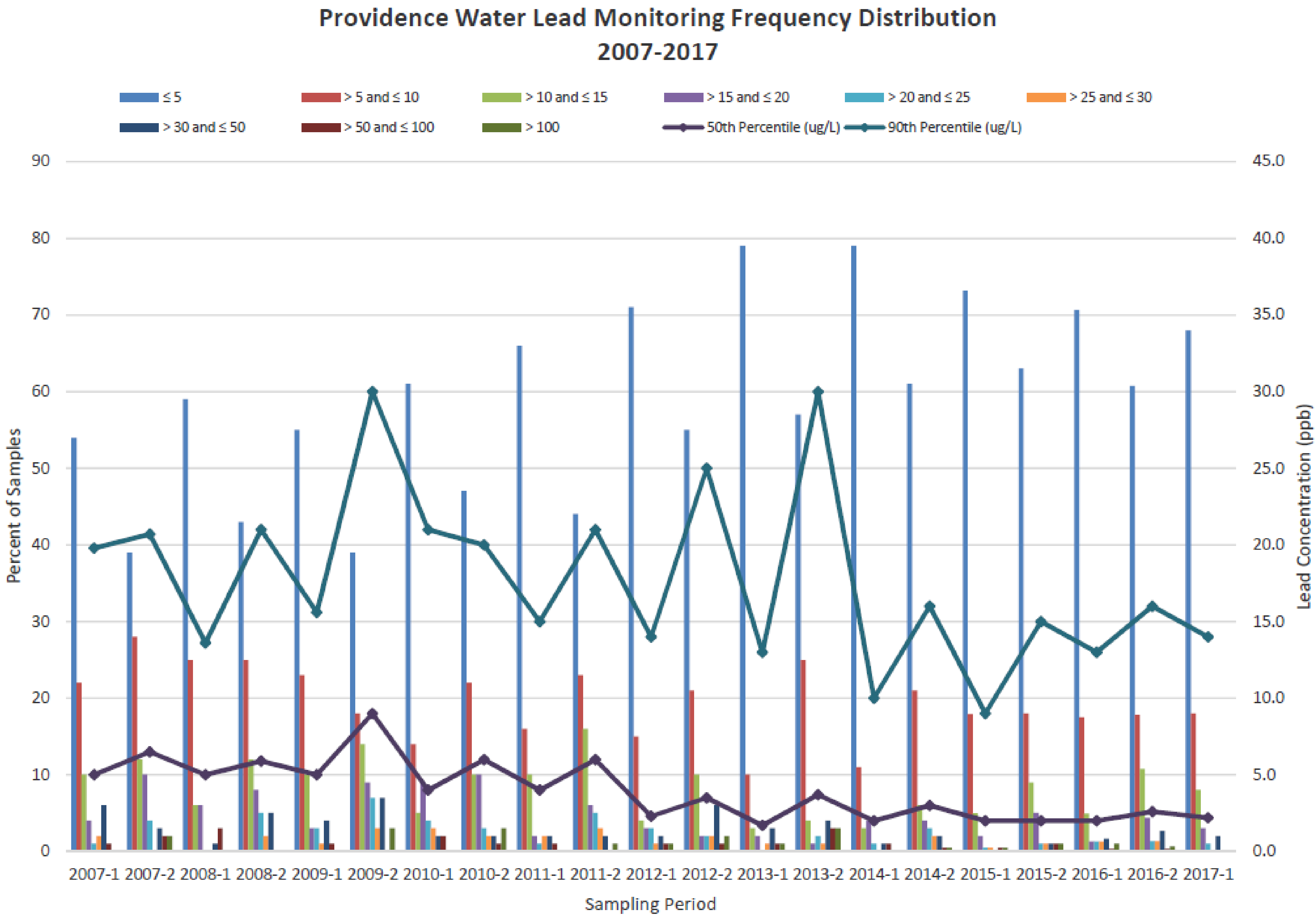
- Overview of Lead in Tap Water
- Flint Water Crisis – Interrupted Corrosion Control
- DC Water Crisis - Response to a Change in Disinfectant
- **Providence – Use of Phosphate for a High pH System**
- Conclusions

Providence, Rhode Island

- Old city with many lead service lines and sections of unlined cast iron water distribution mains.
- Timeline
  - Before 2006: pH 10.2-10.3, Lead 90th percentile = 10-14 µg/L
  - November 2005: lowered pH from 10.2 to 9.7 in an effort to minimize lead solubility, but then had problems with iron corrosion and the lead 90th percentile exceeded 15 µg/L
  - 2012: pH raised back to 10.2-10.3, and lead 90th percentile concentrations have hovered around 15 µg/L.
- Exploring phosphate addition for corrosion control, which is widely used for pH 7-8 but unexplored for high pH systems.

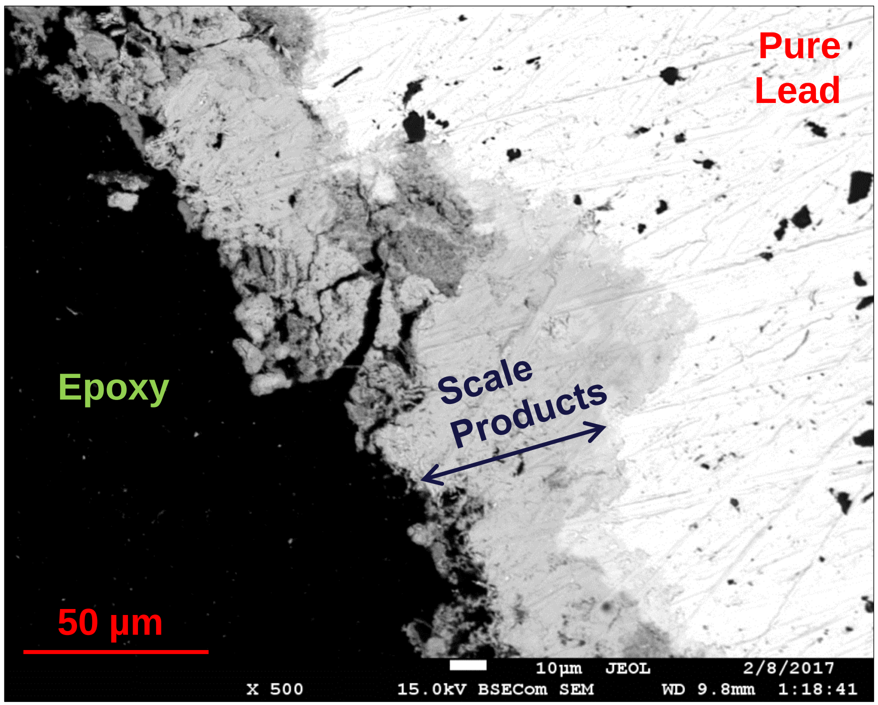


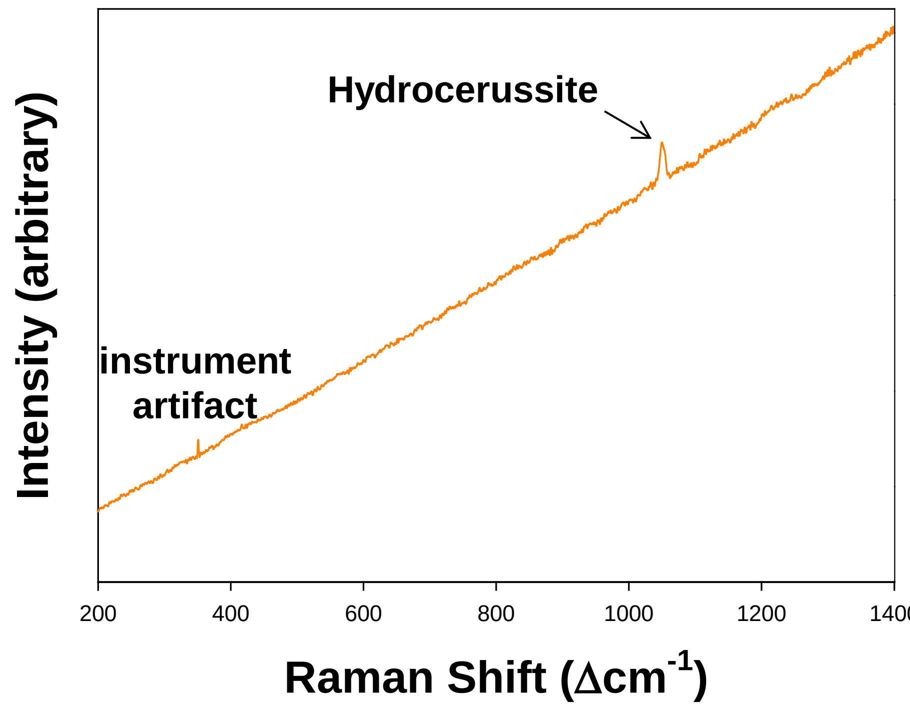
Providence Water Lead Monitoring Frequency Distribution
1997-2006
≤ 5
> 5 and ≤ 10
> 10 and ≤ 15
> 15 and ≤ 20
> 20 and ≤ 25
> 25 and ≤ 30
> 30 and ≤ 50
> 50 and ≤ 100
> 100
50th Percentile (ug/L)
90th Percentile (ug/L)
Percent of Samples
Lead Concentration (ppb)
0
10
20
30
40
50
60
70
80
90
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
1992-1
1992-2
1997-1
1997-2
1998 (RED)
1999 (RED)
2000 (RED)
2000
2003 (RED)
2005 (RED)
2006 (RED)
Sampling Period



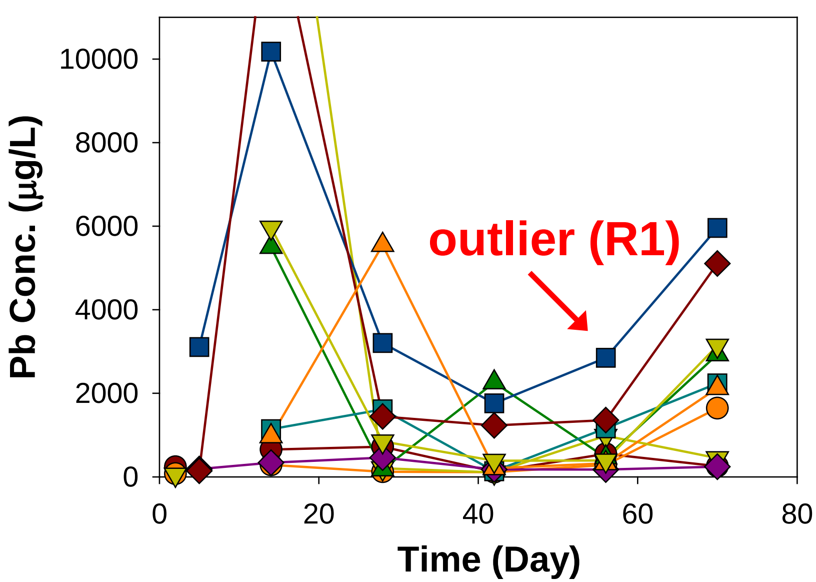
Providence Water Lead Monitoring Frequency Distribution
2007-2017
≤ 5
> 5 and ≤ 10
> 10 and ≤ 15
> 15 and ≤ 20
> 20 and ≤ 25
> 25 and ≤ 30
> 30 and ≤ 50
> 50 and ≤ 100
> 100
50th Percentile (ug/L)
90th Percentile (ug/L)
Percent of Samples
Lead Concentration (ppb)
Sampling Period
0 10 20 30 40 50 60 70 80 90
0.0 5.0 10.0 15.0 20.0 25.0 30.0 35.0 40.0 45.0
2007-1 2007-2 2008-1 2008-2 2009-1 2009-2 2010-1 2010-2 2011-1 2011-2 2012-1 2012-2 2013-1 2013-2 2014-1 2014-2 2015-1 2015-2 2016-1 2016-2 2017-1

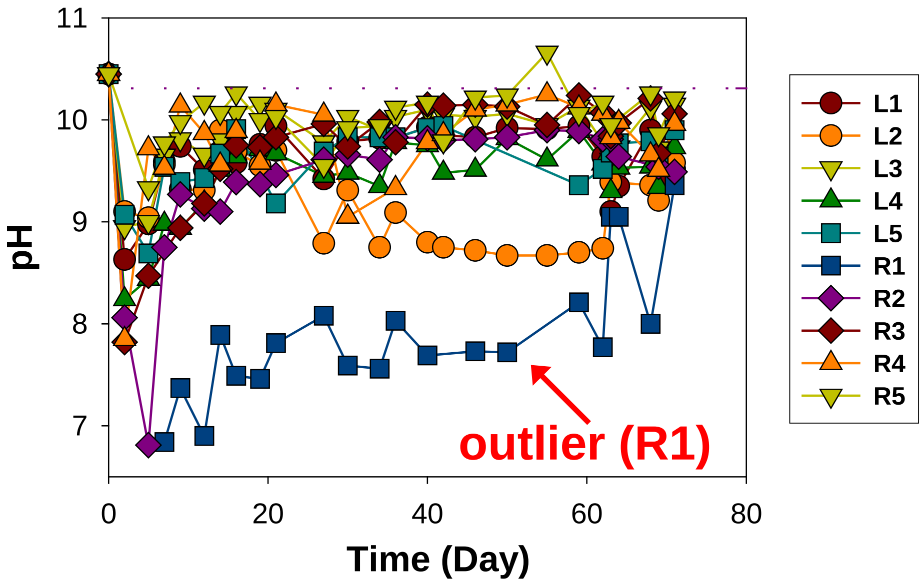
Providence Pipe Scales





Lead Pipe Conditioning

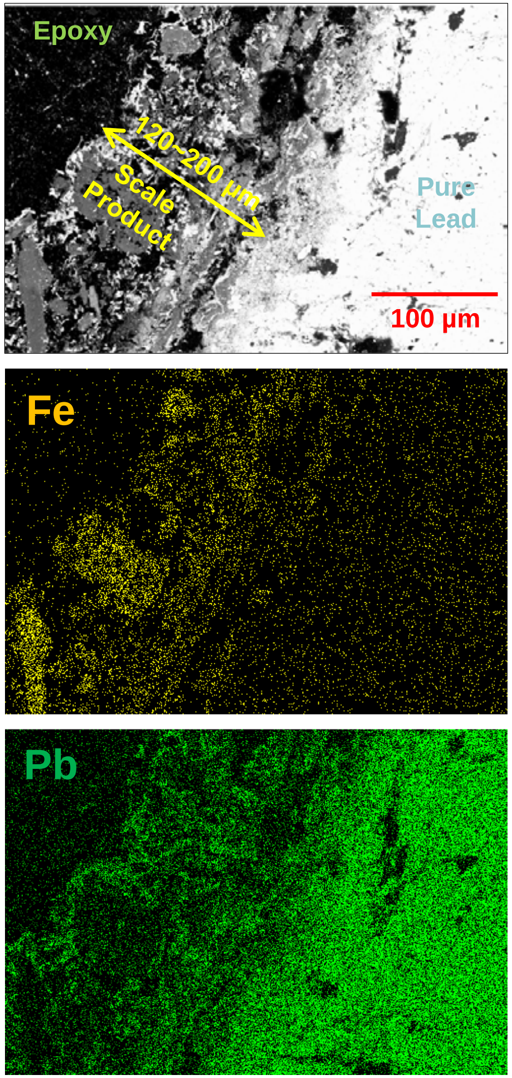




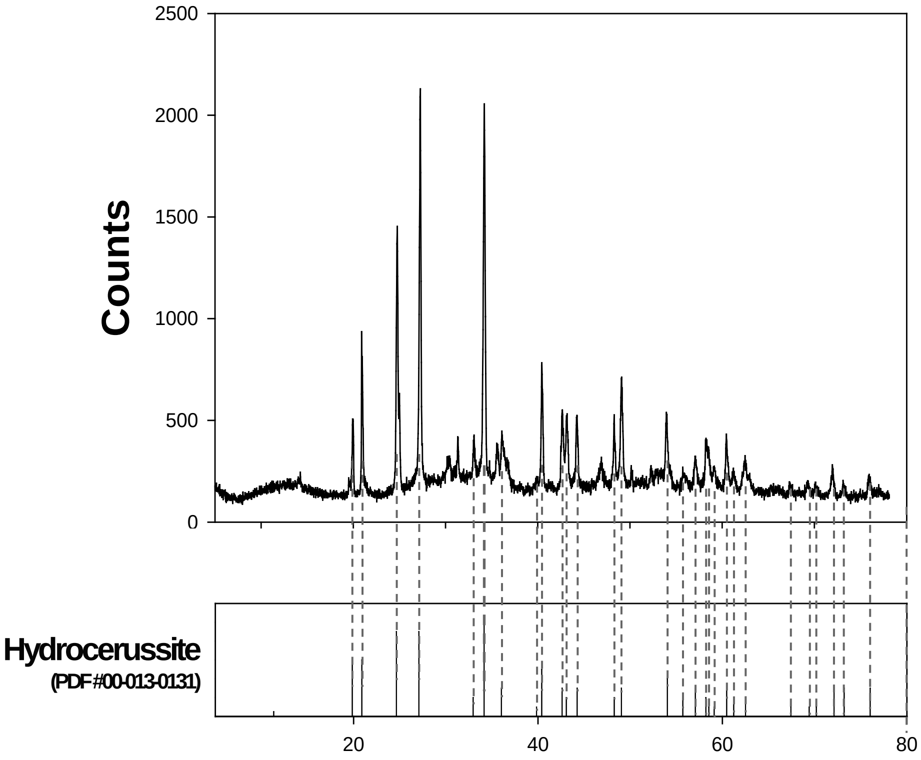
- During fill-and-dump conditioning, Pipe R1 was a clear outlier.
- It was not among the six lead pipes selected for flow-through conditioning and experiments.

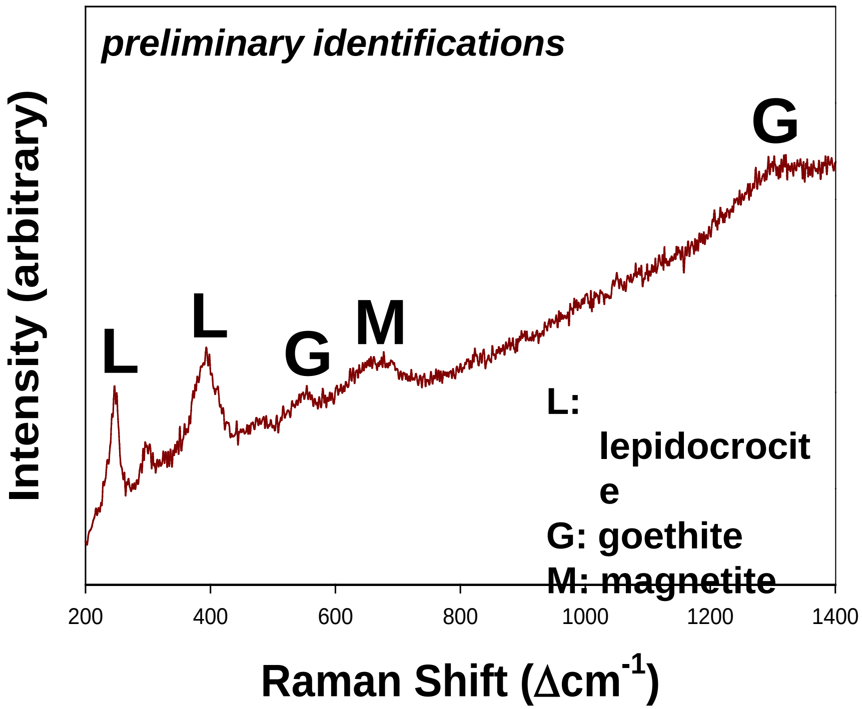
Pipe R1 had iron oxide deposits

- Visibly different than other pipe inner surfaces.
- Pipe scale has a thick (200 µm) layer of iron oxide rich materials.



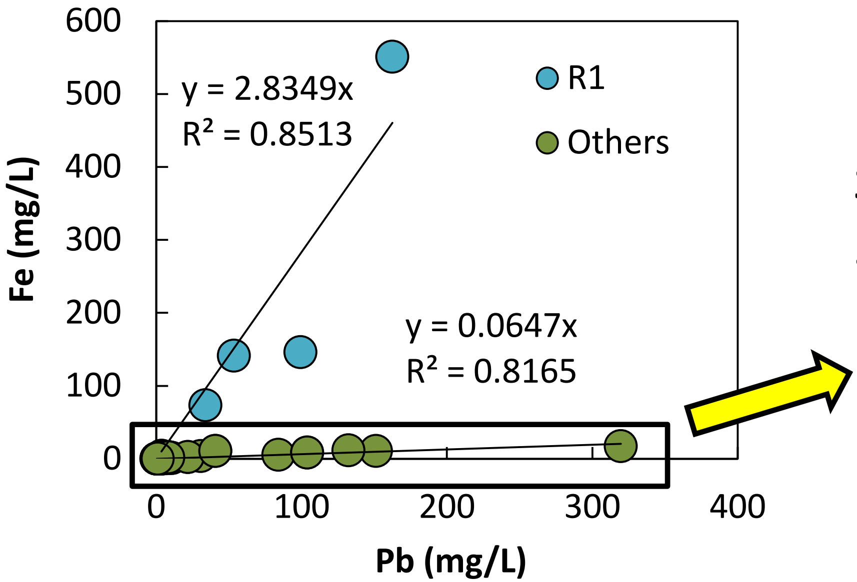
Pipe R1 had iron oxides and hydrocerussite

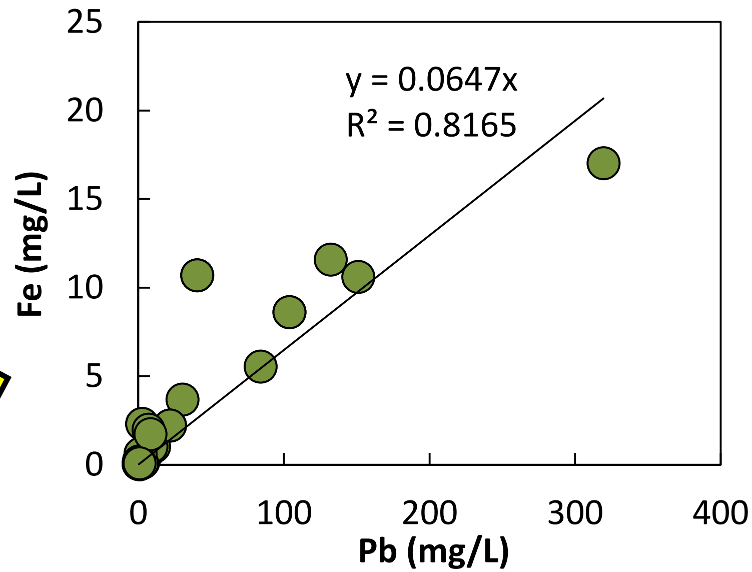




- XRD result suggests a thin layer of Pb is hydrocerussite ($Pb_3(CO_3)_2(OH)_2$).
- Raman peaks indicate a mixture of iron oxides and oxyhydroxides.

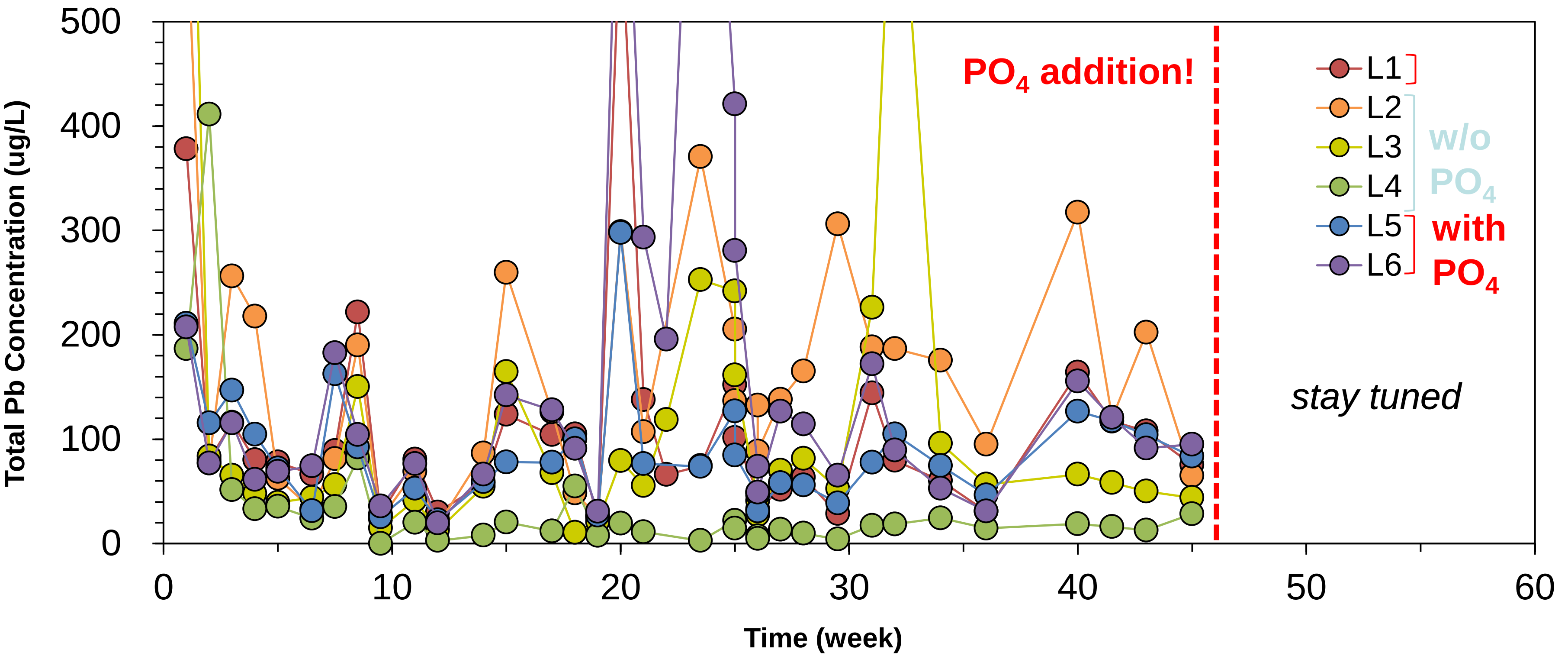
Relationship between iron and lead





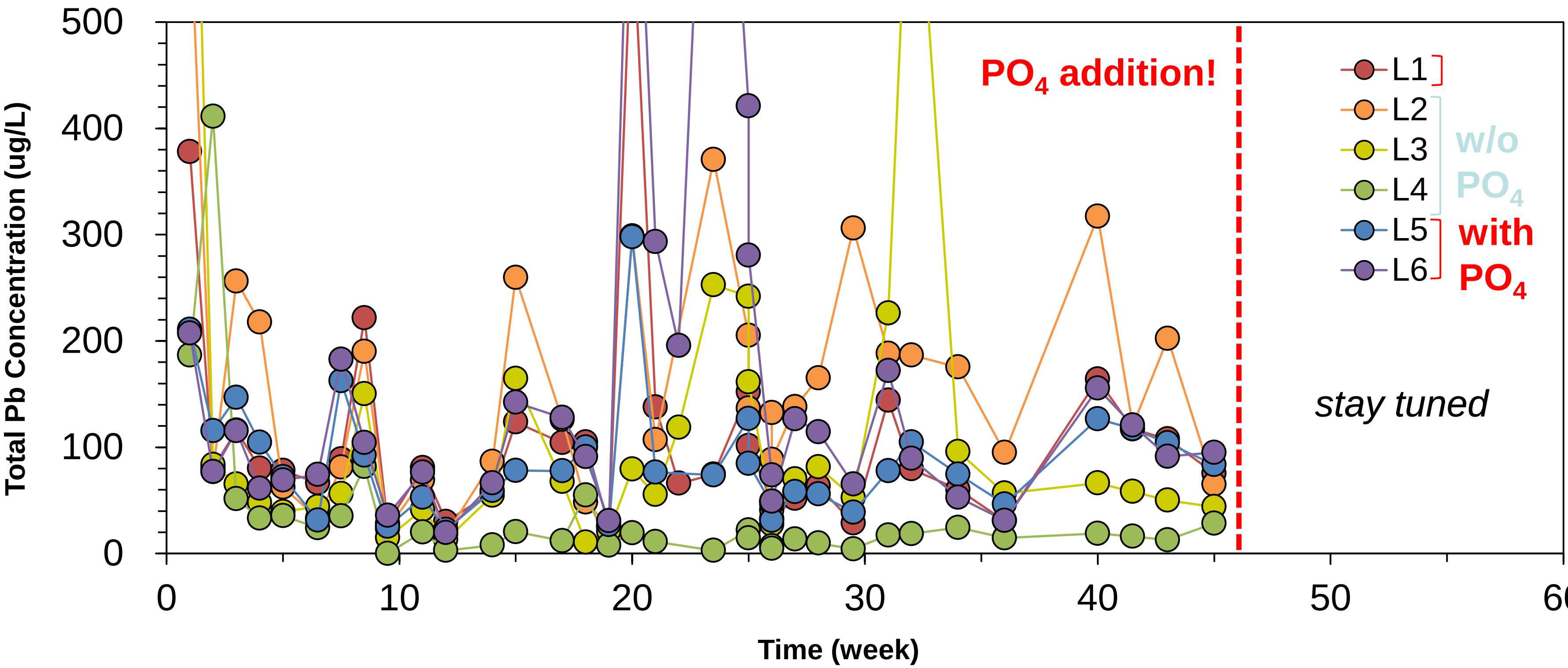
- The Fe/Pb ratio was much higher in samples from the pipe segment with the iron oxide deposits.
- For all pipe segments the iron and lead concentrations were correlated.

Lead Pipe Conditioning with Flow



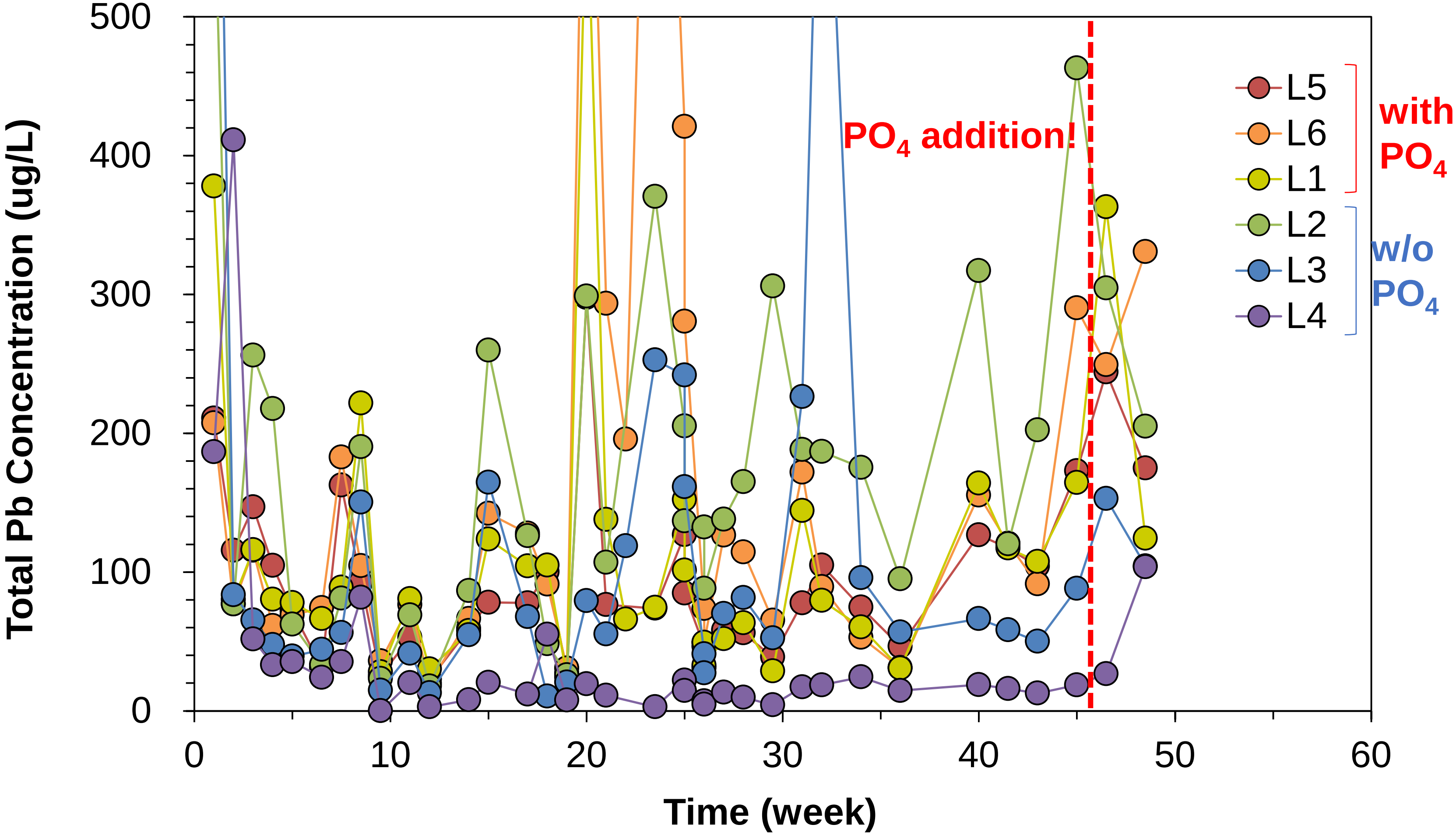
- Pipe L4 has consistently lower lead release than others.
- Analysis of water samples indicated that this pipe had considerable antimony alloyed with lead.

Lead Pipe Conditioning with Flow



- Pipe L4 has consistently lower lead release than others.
- Analysis of water samples indicated that this pipe had considerable antimony alloyed with lead.

Lead Pipe Conditioning and Phosphate Addition

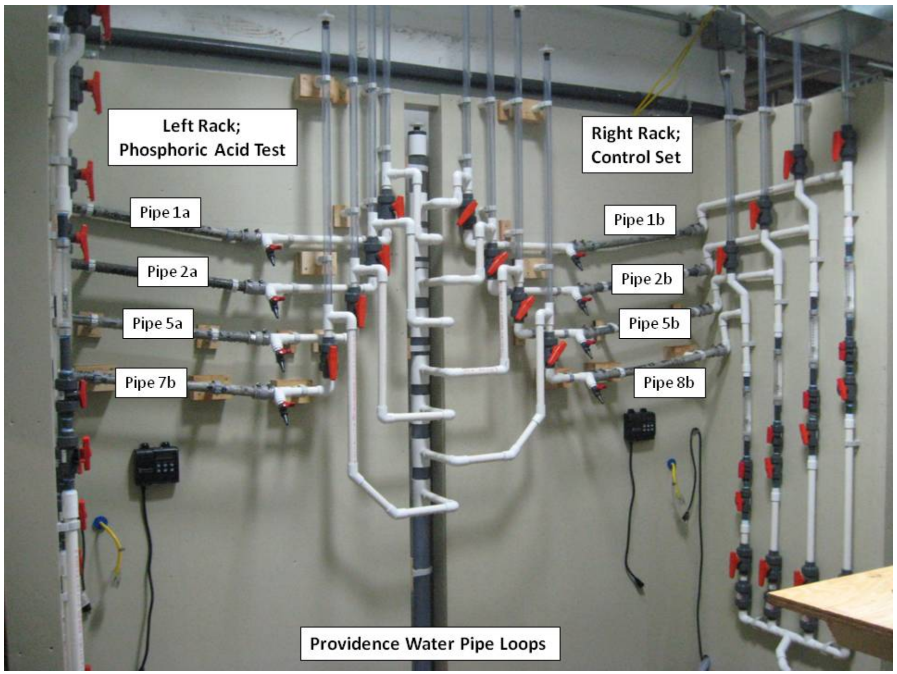


- No clear trends yet in total lead release with and without phosphate.
- Pipe L4 has consistently lower lead release than others; analysis of water samples indicated that this pipe had considerable antimony alloyed with lead.

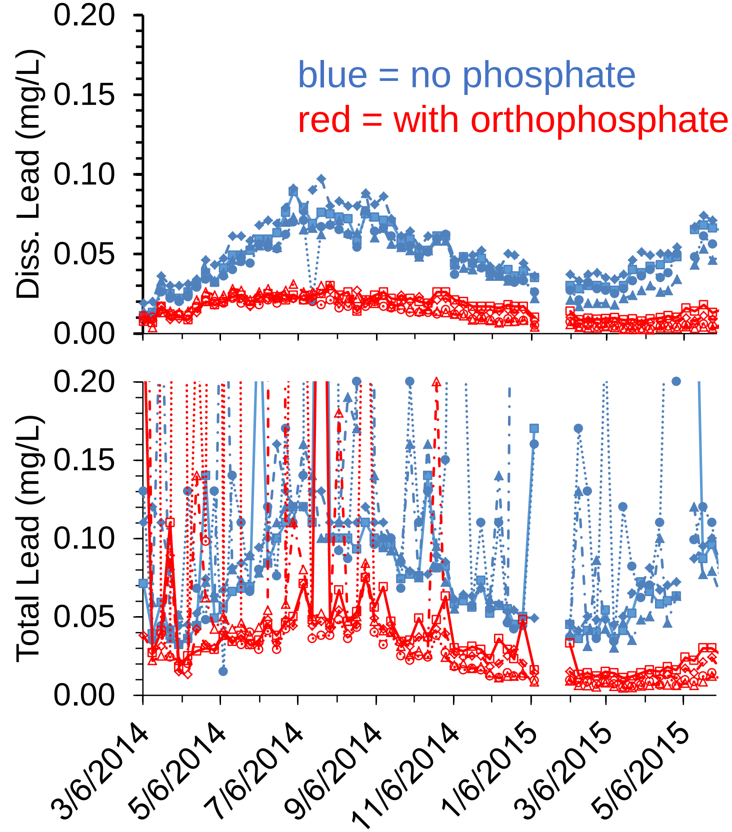
Time for Phosphate to become Effective

Pilot-Scale Investigation in Providence, Rhode Island

- Considering addition of phosphate at a relatively high pH value (~10.3).
- Dissolved lead dropped rapidly.
- Total lead was lower within three months but remained noisy for 9-12 months.



Source: Welter, Schock, Miller, Razza, and Giammar, *WQTC* 2015 Conference Proceedings



Key Findings with High pH System

- Most pipes have scales of hydrocerussite and plumbonacrite.
- For one of the pipes, an iron-rich cake can result in very high lead concentrations.
- Lead-antimony alloy releases less lead than other pipes.
- Orthophosphate has the potential to control lead release even at high pH.
- The pilot-scale tests are continuing and a partial system test with phosphate treatment to a portion of the distribution has been started.

Summary of Lead Corrosion Control

- Lead pipe scales are sensitive to changes in water chemistry.
- The elevated lead levels in Flint were caused by interrupted corrosion control together with a switch in water source.
- A switch from free chlorine to monochloramine results in a dramatic release of lead from PbO_2-rich pipe scales, but this can be mitigated by addition of phosphate before the switch.
- The effectiveness of lead corrosion control can be strongly affected by control of iron corrosion.
- Phosphate can be effective over a wide range of pH.

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