Updated: 29 April 2020

Print version

CEE 680: Water Chemistry

Lecture #50

Redox Chemistry: Lead I

(Stumm & Morgan, Chapt.8)

Benjamin; Chapter 9

Case study: Lead

- Regulations
  - 0.015 mg/L action level in drinking water
- Sources
  - Natural: lead minerals
  - Industrial: paints
  - Plumbing: service connections, solder, brass alloy faucets
- Health Effects
  - Kidney, nervous system damage

A short history of Lead

- Emperor Nero & others
  - a predilection to lead-tainted diets and suffered from gout and other symptoms of chronic lead poisoning
    - Not only did the Romans drink legendary amounts of wine, but they flavored their wines with a syrup made from simmered grape juice that was brewed in lead pots. The syrup was also used as a sweetener in many recipes favored by Roman gourmands.
    - "One teaspoon of such syrup would have been more than enough to cause chronic lead poisoning," Dr. Nriagu said.

Peter Ustinov as Nero

NY Times: March 17, 1983

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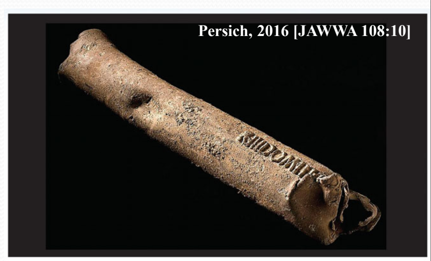
Our continuing love affair with lead

- Used for some of the earliest pressurized water pipes
  - Malleable, plentiful
  - Plumbing and plumbers use Pb
- Used with modern urban water systems
  - Lead service lines – esp. 1920s-1940s
  - Lead solder: until 1986
  - Brass fittings with lead



Roman lead water pipe, 81–96 CE. *Source: Science Museum, London, 2014; Wellcome Images, CC BY 4.0.*

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Then, Flint

Flint

- 31 January 2016; Boston Globe

A6 The Nation BOSTON SUNDAY GLOBE

Flint worries are focused on children

Doctor believes lead may have harmed 8,000

By Abby Goodnough
NEW YORK TIMES

BRITTANY GREESON/NEW YORK TIMES

Dr. Mona Hanna-Attisha examined 2-month-old Taeyana Brown, in Flint, Mich.

FLINT, Mich. — Quayana Towns' 2-month-old daughter wriggled on an exam table last week as her pediatrician ticked off questions that have become essential for every parent of young children here.

"So what are you guys doing for water — what are you drinking?" asked the doctor, Mona Hanna-Attisha.

"I have a whole bunch of bottled water that I picked up," said Towns, 26, assuring the doctor that the family had been drinking it for a few months, since the gravity of Flint's water crisis came to light.

"And before that you were using tap water?"

"Yes," Towns replied, as her other child, a 1-year-old, King, toddled around.

Hanna-Attisha would waste no time adding King and his sister, Taeyana, to a new database of children under 6 who may have been exposed to lead in Flint's water, a group she believes could number 8,000.

Of all the concerns raised by the contamination of Flint's water supply, and the failure of the state and federal governments to promptly address the crisis after it began nearly two years ago, none is more chilling than the possibility that children in this tattered city may have suffered irreversible damage to developing brains and nervous systems from exposure to lead.

Residents and advocates have expressed outrage over the government's failure to protect Flint's children, something many of them say would not have happened if the city were largely white. Adding to their injury, they say, are the harsh conditions of poverty that have already placed ample obstacles in their young lives.

At the same time, many are turning their attention to the future, when the effects of consuming lead-laced water for months may be all too evident.

At the center of those efforts is Hanna-Attisha, whose research documenting a spike in children's blood lead levels forced dismissive government officials to finally acknowledge the water crisis last fall. With her colleagues at Hurley Children's Hospital, where she directs the pediatric residency program, she is at the forefront of the scramble to put in place the services and resources so that every child who needs extra help learning or overcoming medical problems will have support for years to come.

Decades of research have found that exposure to even low levels of lead can profoundly affect children's growth, behavior, and intelligence over time. Studies have linked elevated lead levels in blood to learning disabilities, problems with attention and fine motor coordination, and even violent behavior.

Younger children and fetuses are especially vulnerable because of their developing brains and nervous systems, which is why the efforts here will focus on children 5 and younger.

Eemails released by the office of Governor Rick Snyder last week referred to a resident who said she was told by a state nurse in January 2015, regarding her son's elevated blood lead level, "It is just a few IQ points. . . . It is not the end of the world."

Hanna-Attisha and others who have studied lead poisoning have a sharply different view of lead exposure, for which there is no cure.

"If you were going to put something in a population to keep them down for generations to come, it would be lead," Hanna-Attisha said.

Underlying the problem are the troubling conditions prevalent among low-income children and their families in cities like Flint: spotty access to doctors and health care services; a dearth of healthy foods; living conditions so poor that many of the children may have already been exposed to lead poisoning from the paint in their homes; parents with limited time and financial resources.

The doctors here said they will focus on improving the diets of affected children and expanding education programs like Head Start, the federally funded preschool program for low-income children, which already has a waiting list in Flint. Hanna-Attisha has submitted dozens of recommendations to the governor, state legislators and federal officials.

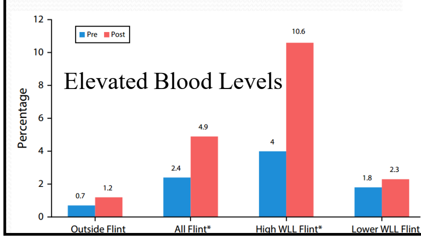
It remains a wish list at this point, but she and others believe that with Flint's public health crisis in the national spotlight, the city's chances of getting help are better than ever before.

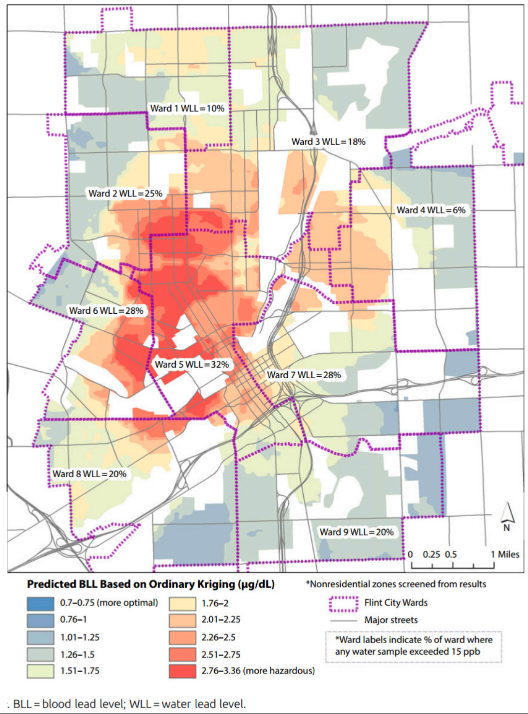
Snyder and the state Legislature have so far allocated $28 million in emergency state spending for Flint. Some of the money will provide initial services, like health assessments and home visits from nurses, to lead-exposed children. Snyder has also asked the federal government to expand Medicaid to cover every Flint resident younger than 21, regardless of income level. And Democrats in Congress said Thursday that they would seek $600 million in federal aid for Michigan to help Flint.

Blood Pb

- Children <5 yrs
- Levels in 2015; after change to Flint River

Hanna-Attisha et al., 2016
AJPH 106:2:283-290





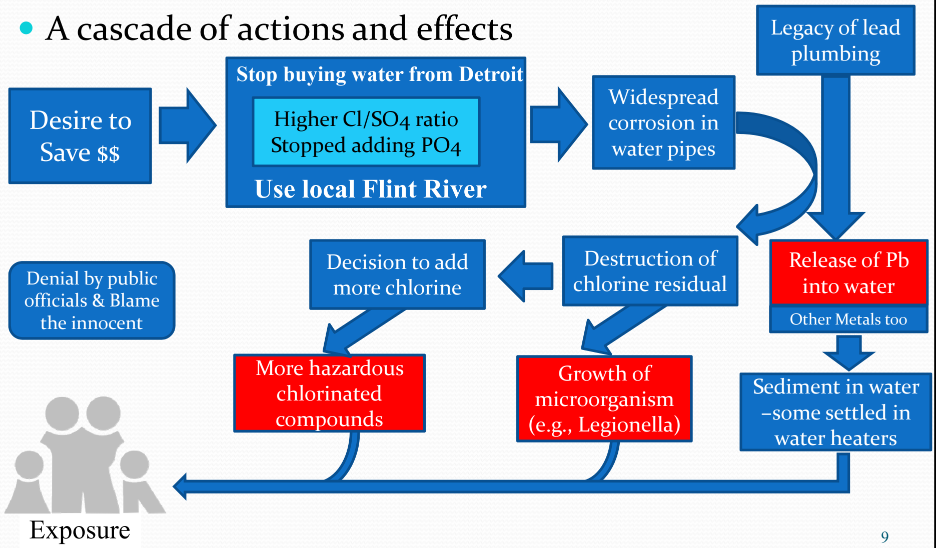
. BLL = blood lead level; WLL = water lead level.

Flint Michigan Crisis

- Timeline
  - April 2014: the city stopped getting its water from Detroit as a cost-saving measure and began instead drawing water from the Flint River.
  - High blood lead levels noted in children
  - Water led levels were above standard
  - Oct 16, 2015: Flint switches back to Detroit Water
- Sources
  - EPA website: http://www.epa.gov/flint/flint-drinking-water-documents
  - VPI website: http://flintwaterstudy.org/
  - 12/22/2015 Rachel Maddow video:

The Flint case

- A cascade of actions and effects



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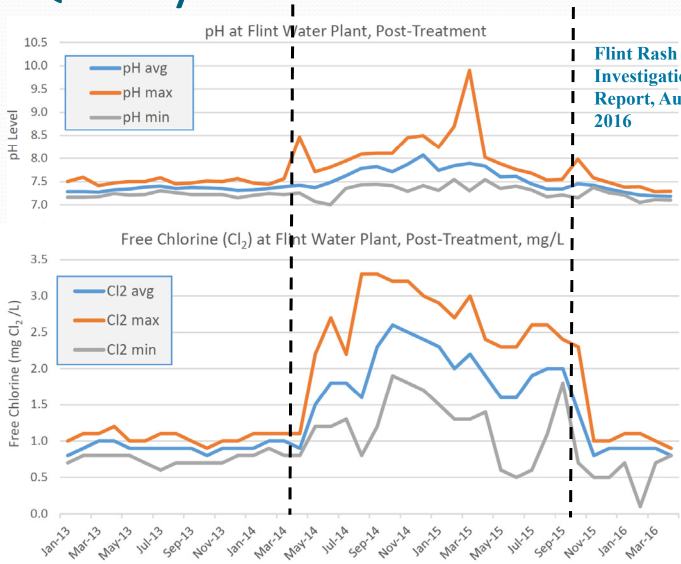
Water Quality

Period on Flint River

- pH
- Cl2



Flint Rash Investigation Report, August, 2016

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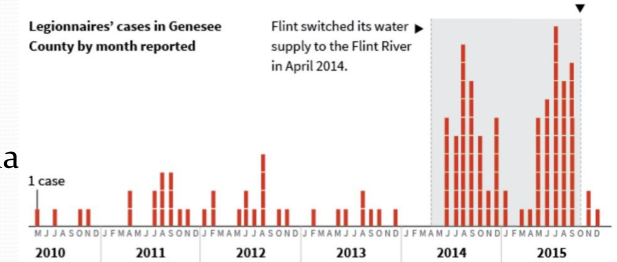
Other issues

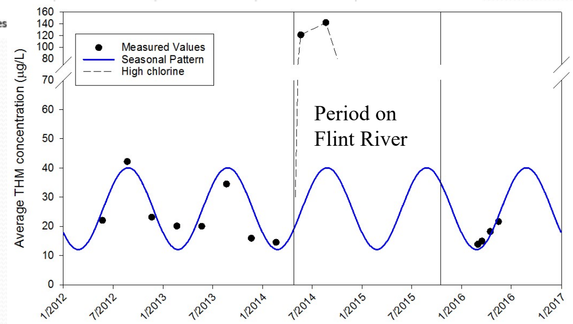
- Legionella

From Huffington Post, http://www.huffingtonpost.com.au/entry/flint-water-legionnaires-lead-crisis_us_569d09d6e4b0ce4964252c33



- Trihalomethanes

Flint Distribution system locations; data from WITAF, EPA and UMass



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The press & public reaction

- Cites elevated DBPs in water heaters
  - Ruffalo advises against bathing
  - video

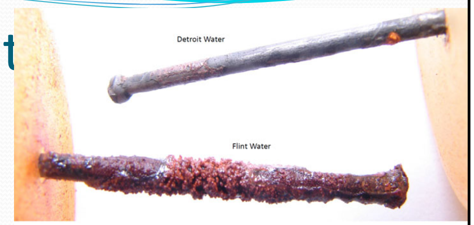
May 4, 2016

May 5, 2016

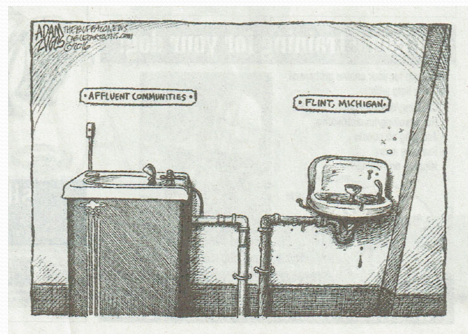
May 31, 2016

Public engagement

- Edwards slide
- Environmental justics issues



Steel Exposed One Month to Detroit vs. Flint River Water



Protection by a $CaCO_3$ film?

- Calcium carbonate will precipitate when the solubility product is exceeded
  - This occurs at elevated pHs where the equilibrium shifts toward more carbonate
  - Of course there has to be a certain amount of calcium (hardness present as well)
- This film has been shown to protect pipes from corrosion
  - for this reason, high pHs and high alkalinities can help with corrosion control
  - How high should the pH be?

See lecture #39

Me-Carbonate Equilibria

- From Pankow

$MCO_{3(s)} = M^{2+} + CO_3^{2-}$ $K_{s0} = [M^{2+}][CO_3^{2-}]$ (12.1)

$M^{2+} + OH^- = MOH^+$ $K_{H1} = \frac{[MOH^+]}{[M^{2+}][OH^-]}$ (12.2)

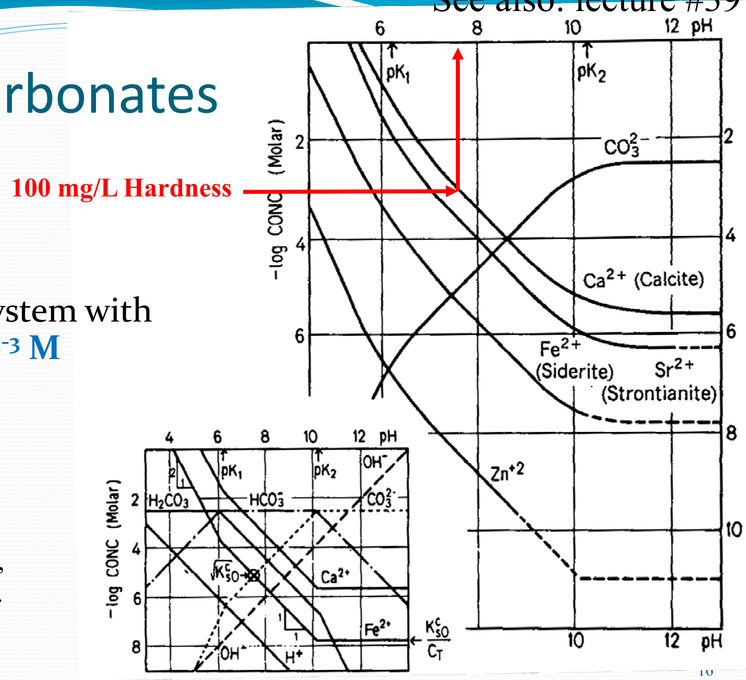
$MOH^+ + OH^- = M(OH)_2^o$ $K_{H2} = \frac{[M(OH)_2^o]}{[MOH^+][OH^-]}$ (12.3)

$M(OH)_2^o + OH^- = M(OH)_3^-$ $K_{H3} = \frac{[M(OH)_3^-]}{[M(OH)_2^o][OH^-]}$. (12.4)

Metal Ion	$\log K_{s0}$	$\log K_{H1}$	$\log K_{H2}$	$\log K_{H3}$	pH for initially-pure water (i.e., $(C_B' - C_A') = 0$) in equilibrium @ 25°C/1 atm with a divalent metal carbonate. exactly using Eq. (12.17)	approximately using Eq. (12.26)
Mg^{2+}	−7.46	2.58	–	–	10.19	10.29
Ca^{2+}	−8.30	1.3	–	–	9.96	10.01
Ba^{2+}	−8.30	0.64	–	–	9.96	10.01
Sr^{2+}	−9.03	0.82	–	–	9.73	9.77
Mn^{2+}	−9.30	3.4	3.4	1.0	9.63	9.68
Zn^{2+}	−10.00	5.0	6.0	2.5	9.24	9.44
Fe^{2+}	−10.68	4.5	2.9	2.6	8.93	9.22
Pb^{2+}	−13.13	6.3	4.6	3.0	8.20	8.40
Cd^{2+}	−13.74	3.9	3.8	2.6	7.88	8.20

See also: lecture #39

Me-carbonates



- Closed System with $C_T = 3x10^{-3}$ M

Stumm & Morgan, 1996, Figure 7.8, pg. 374

Langelier Index (LI)

- A measure of the degree of saturation of calcium carbonate in water
  - When a water is exactly in equilibrium with $CaCO_3$ such that neither dissolution nor precipitation is occurring,
    - LI = 0
  - When $CaCO_3$ precipitation is occurring, the water is oversaturated and by definition:
    - LI >0
  - So the extent of oversaturation (ie., the LI) is defined as the number of log units of the actual, measured, water pH (pH_{act}) above the theoretical value that gives perfect equilibrium (pH_{sat})

$$LI \equiv pH_{act} - pH_{sat}$$

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LI continuted

- The saturation pH can be calculated using the solubility product constant (Kso) and knowing the water's carbonate content from knowledge of the alkalinity

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No assumptions on mass balance

- Returning to the basic solubility, but not requiring that calcium and total carbonates be equal

$$K_{so} = [Ca^{+2}][CO_3^{-2}]$$

$$K_{so} = [Ca^{+2}]\alpha_2 C_T$$

$$\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$

And so at pH = 6.3 – 10.3

$$\alpha_2 \approx \frac{1}{\frac{[H^+]}{K_2}} = {}^{K_2}/_{[H^+]}$$

$$K_{so} = [Ca^{+2}]\frac{K_2}{[H^+]}C_T$$

$$[H^+] = [Ca^{+2}]\frac{K_2}{K_{so}}C_T$$

LI (cont)

- Continuing

$$[H^+] = [Ca^{+2}]\frac{K_2}{K_{so}}C_T$$

$$log\,[H^+] = log[Ca^{+2}] + logK_2 - logK_{so} + logC_T$$

$$pH_{sat} = -log[Ca^{+2}] + pK_2 - pK_{so} - logC_T$$

- And now combining with the LI definition

$$LI \equiv pH_{act} - pH_{sat}$$

$$LI = pH_{act} + log[Ca^{+2}] - pK_2 + pK_{so} + logC_T$$

LI (cont)

- And since in the pH range below 10.3, the alkalinity is mostly due to bicarbonate, we can equate the C_T to the alkalinity

$$LI = pH_{act} + log[Ca^{+2}] - pK_2 + pK_{so} + log[Alk]$$

- And general practice has been to increase pH so that the LI is 0.2 to 1.0
- While CaCO3 films have been found to inhibit iron corrosion, there is little evidence that a high LI can reduce the level of soluble Pb

Flint Water Quality – why?

Parameter	Before 4/2014	After 4/2014	units
pH	7.38	7.61	
Hardness	101	183	mg-CaCO3/L
Alkalinity	78	77	mg-CaCO3/L
Chloride	11.4	92	mg/L
Sulfate	25.2	41	mg/L
CSMR	0.45	1.6	mg/mg
Inhibitor	0.35	None	mg-P/L
Larson Ratio	0.5	2.3	

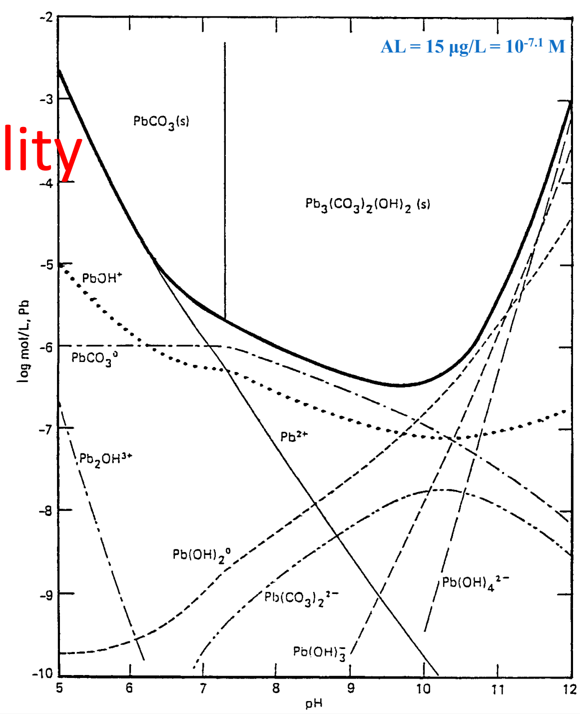
WQ data From MOR and 2014 WQR
CSMR = chloride to sulfate mass ratio
Larson Ratio = ($[Cl^-] + 2[SO_4^{-2}]$)/$[HCO_3^-]$

Pb(II) solubility

- 3 mg/L DIC
- No phosphate

But how does Pb(II) get into drinking water in the first place?

From: Internal Corrosion and Depositional Control, by Schock & Lytle, Chapt. 20 in Water Quality and Treatment (6th ed.), 2011



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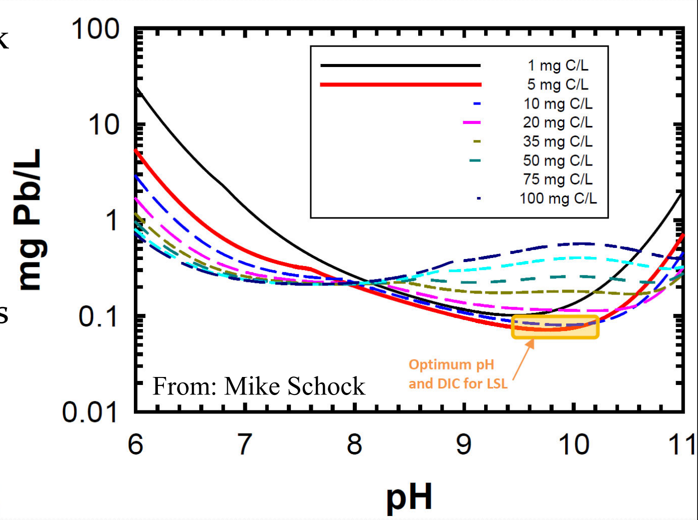
Control w/o Phosphate or high Redox

- Can only work for low carbonate waters
- Not as good as phosphate or high Redox



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Flint Finished Water Quality – why?

Alkalinity was about the same; pH actually went up a bit

Parameter	Before 4/2014	After 4/2014	units
pH	7.38	7.61	
Hardness	101	183	mg-CaCO3/L
Alkalinity	78	77	mg-CaCO3/L
Chloride	11.4	92	mg/L
Sulfate	25.2	41	mg/L
CSMR	0.45	1.6	mg/mg
Inhibitor	0.35	None	mg-P/L
Larson Ratio	0.5	2.3	

WQ data From MOR and 2014 WQR
CSMR = chloride to sulfate mass ratio
Larson Ratio = $([Cl^-] + 2[SO_4^{-2}])/[HCO_3^-]$

WQ data from Edwards website

Consider galvanic corrosion

- Micro environments near surface can have very low pHs
  - Basic ligands like hydroxide and phosphate will be much less important
  - Weak base anions can become enriched

Nguyen et al., 2010; WRF Report

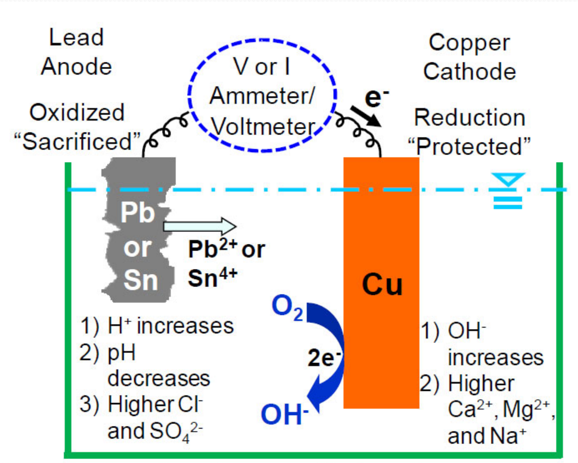

Figure 1.1 Reactions at lead anode and copper cathode surfaces

Sulfate and Chloride

- In bulk water neither sulfate nor chloride can compete well with hydroxide for lead
- Near surface with active galvanic corrosion, pH drops and hydroxide is very low
  - Sulfate forms insoluble $PbSO_4$ precipitate

$$K_{so} = [Pb^{+2}][SO_4^{-2}] = 1.54x10^{-8}$$

  - Chloride forms soluble $PbCl^+$ complex

$$K_1 = {[PbCl^+]}/{[Pb^{+2}][Cl^-]} = 59.5$$

Nguyen et al., 2010; WRF Report

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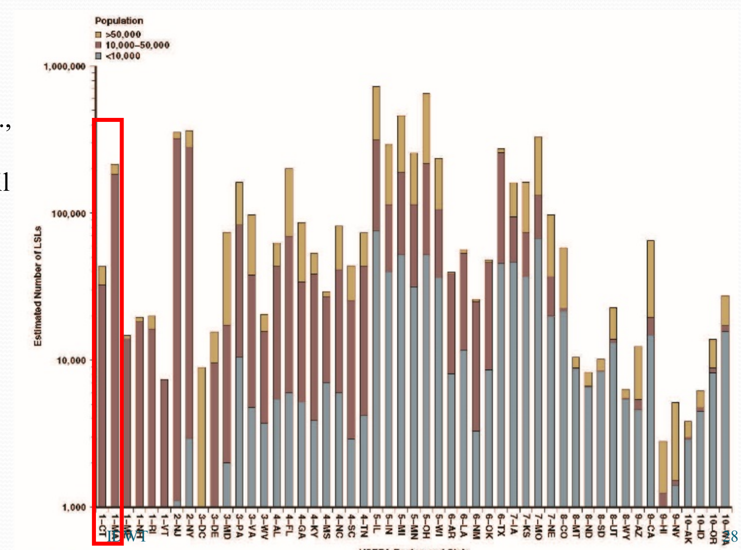
Getting the lead out: Lead service lines (LSL) in US

Cornwall et al., 2016 JAWWA, April



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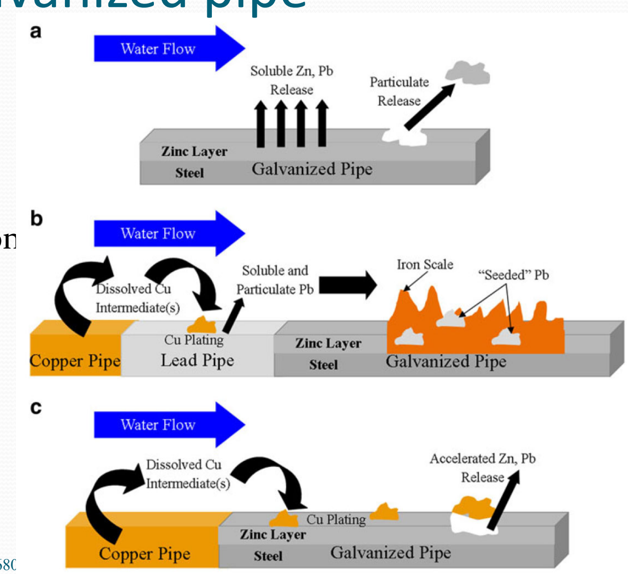
Galvanized pipe

- Widely used to replace lead pipe for service connections
- What is it?
  - Steel coated with zinc to reduce corrosion
  - Zinc used for this coating is generally contaminated with lead
    - 0.5% up to 1.4% Pb by weight

From: Clark, Masters and Edwards, 2015 [Env. Eng. Sci. 32:8:713]

Pb from galvanized pipe

a) Galvanized pipe releases Zn and Pb
b) Pb sorption and deposition in iron scales
c) With Cu pipe, deposition corrosion accelerates release



Iron Scale

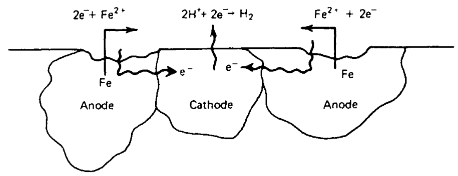


FIGURE 17.1 Adjoining anodes and cathodes during the corrosion of iron in acidic solution. (*Source: Water Chemistry,* V. L. Snoeyink and D. Jenkins. Copyright © 1980, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

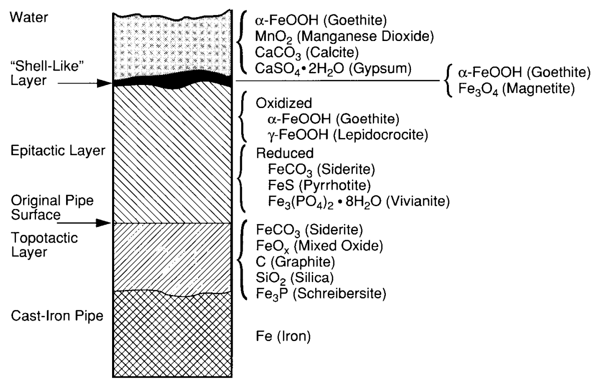
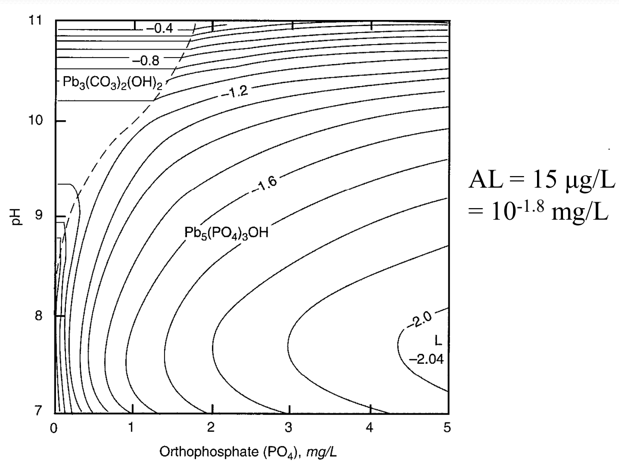


Figure 2-6 Schematic of scale on a cast-iron distribution pipe

Pb(II): pH vs PO_{4T} ;low CO_{3T}

- 6 mg/L DIC

From: Internal Corrosion of Water Distribution System, (2nd ed) by Snoeyink, Wagner et al., 1996



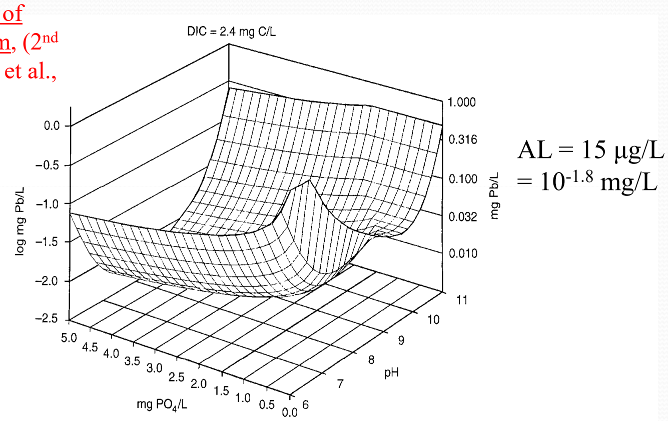
AL = 15 μg/L = $10^{-1.8}$ mg/L

NOTE: Concentration units are log (mg Pb/L). The solid phase boundary lines are approximate.

Figure 4-19 Contour diagram for the impact of varying concentrations of orthophosphate and hydrogen ion, with DIC = 6 mg C/L, temperature = 25°C, and I = 0.005 mol/L

Pb(II); pH/PO_4 contour plot

From: Internal Corrosion of Water Distribution System, (2nd ed) by Snoeyink, Wagner et al., 1996



AL = 15 µg/L = $10^{-1.8}$ mg/L

Figure 4-21 Three-dimensional surface plot of lead concentration versus orthophosphate dose for 2.4 mg C/L DIC (DIC = $2 \times 10^{-4} M$, I = 0.01 mol/L, temperature = 25°C)

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Washington, DC
Pb Increase Correlates with Chloramines

Monitoring Period Start	Monitoring Period End	Lead (ppb) 90th percentile
January 1, 1992	June 30, 1992	**18**
July 1, 1992	December 31, 1992	**15**
January 1, 1993	June 30, 1993	11
July 1, 1993	December 31, 1993	**37**
January 1, 1994	June 30, 1994	14
July 1, 1994	December 31, 1994	12
January 1, 1997	June 30, 1997	6
July 1, 1997	December 31, 1997	8
July 1, 1998	December 31, 1998	7
January 1, 1999	June 30, 1999	5
July 1, 1999	June 30, 2000	12
July 1, 2000	June 30, 2001	8
July 1, 2001	June 30, 2002	**75**
January 1, 2003	June 30, 2003	**40**
July 1, 2003	December 31, 2003	**63**

pH Raised with CaO

NH3 added to give Chloramines

Grumbles & Welsh, WASA, House Testimony 3/5/04

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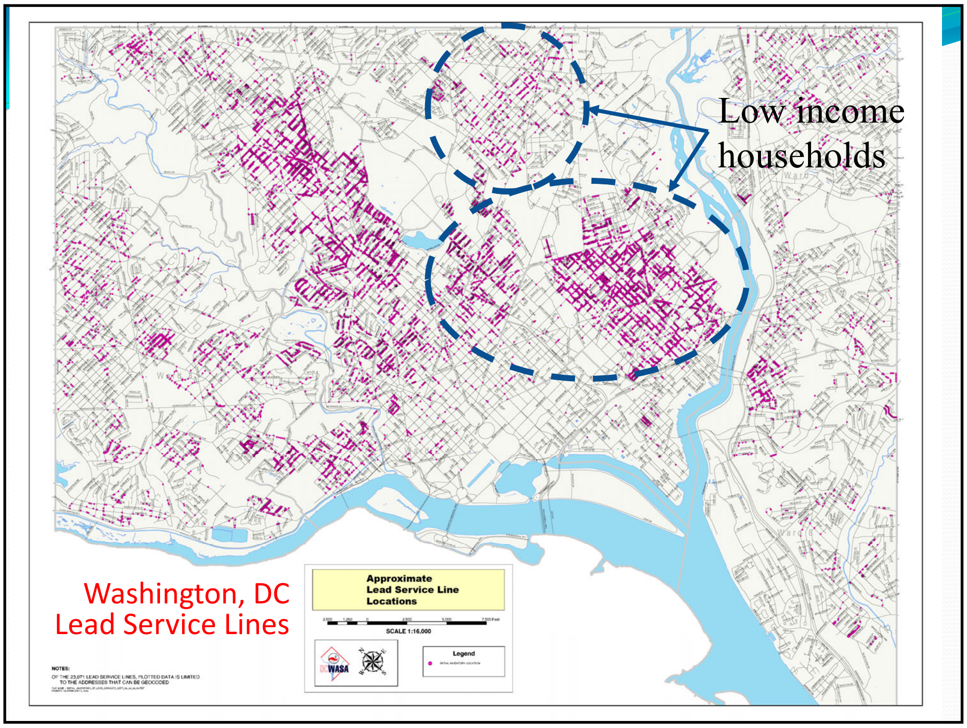
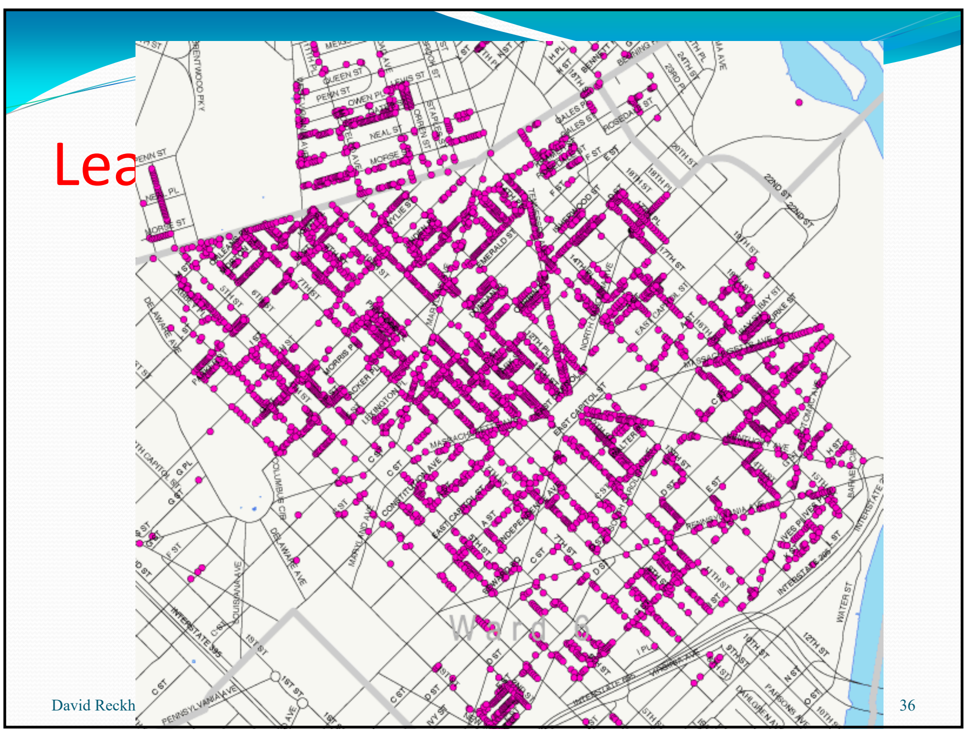

Low income
households
Washington, DC
Lead Service Lines
Approximate
Lead Service Line
Locations
SCALE 1:16,000
Legend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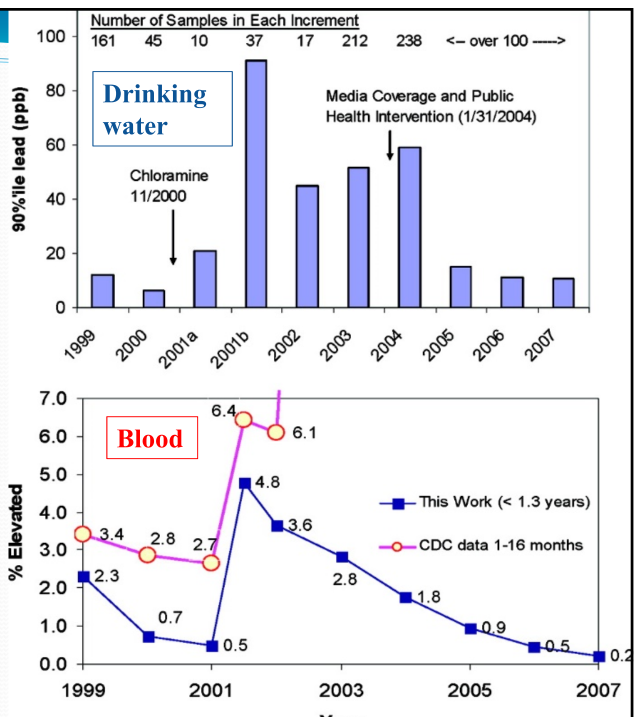
Chloramines: a solution to the DBP problem?

- Inorganic chloramines are formed by the reaction of free chlorine with ammonia.

  $NH_3 + HOCl$ --------> $NH_2Cl + H_2O$ (1)
- Monochloramine is formed very quickly (in minutes)
- Although it is not as powerful an oixidant or disinfectant as free chlorine, it does continue to provide some pathogen protectionl
- It does not continue to produce THMs and most HAAs like free chlorine does
- Therefore, many cities like DC have decided to convert their distribution system disinfectant to chloramines

Washington DC

- Free chlorine and lime addition (high pH)
- Nov 2000, switch to chloramines



Edwards et al., 2009; *Environ. Sci. Technol.*, *43* (5), pp 1618–1623

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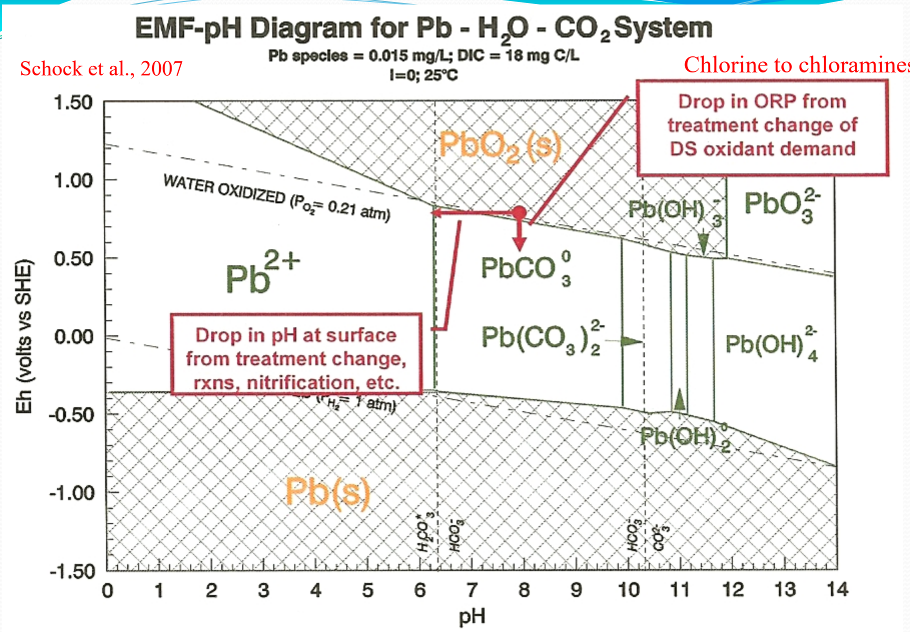

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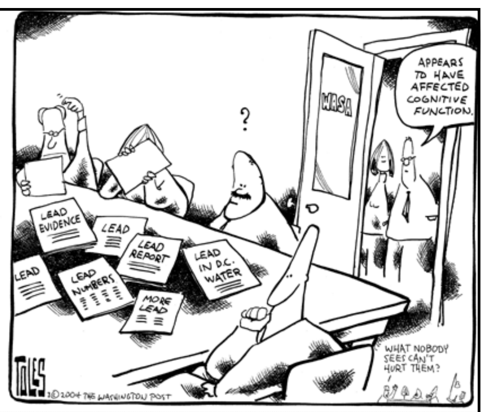
What went wrong?



- Washington, DC
  - Change from chlorine to chloramines
  - Solubilization of lead (+IV)
- Flint, MI
  - Change from low Chloride water to high
  - No more phosphate inhibitor
  - Greater corrosion rates

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How to avoid Lead problems

- Optimized corrosion control treatment
  - Control of pH and alkalinity
  - Addition of orthophosphate based corrosion inhibitors
  - Keep oxidized environment
- Minimize changes in distributed water chemistry
- Removal lead from system
  - Lead service lines
  - Lead in plumbing fixtures

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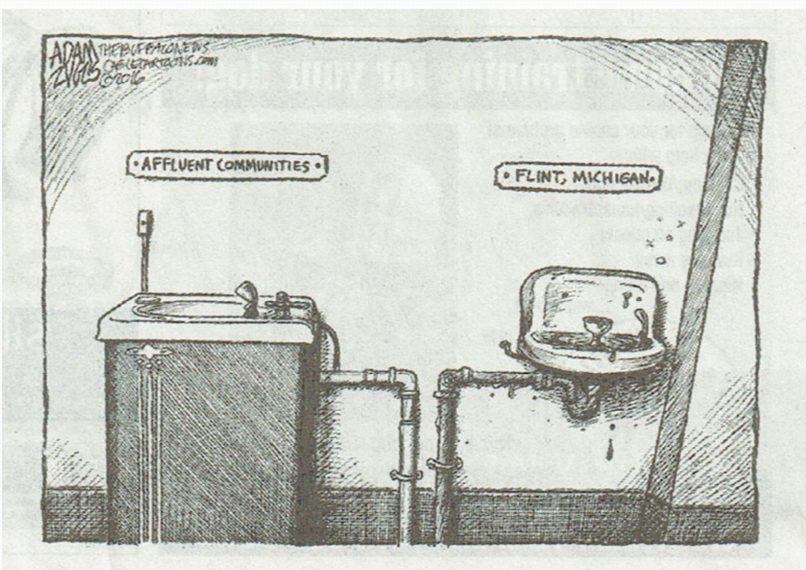
Daily Hampshire Gazette: 22 Jan 2016



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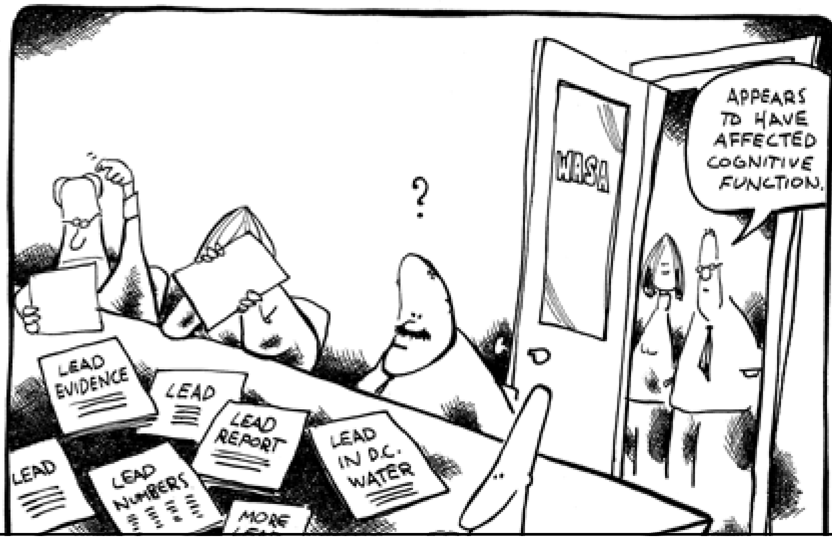
2003 Lead crisis in Washington, DC



NY Times: 27 March 2016

Lead in Water Still Torments Many Schools

*This article is by **Michael Wines, Patrick McGeehan** and **John Schwartz**.*

JERSEY CITY — Anxious parents may wonder how a major school system like Newark's could overlook lead in the drinking water of 30 schools and 17,000 students. The answer: It was easy. They had to look only a few miles away, at the century-old classrooms of the schools here, across the Hackensack River.

The Jersey City Public Schools district discovered lead contamination in eight schools' drinking fountains in 2006, and in more schools in 2008, 2010 and 2012. But not until 2013 did officials finally chart a comprehensive attack on lead, which by then had struck all but six schools.

This winter's crisis in Flint, Mich., has cast new attention on lead in water supplies. But problems with lead in school water supplies have dragged on for years — aggravated by ancient buildings and plumbing, prolonged by official neglect and tight budgets, and enabled by a gaping loophole in federal rules that largely exempts schools from responsibility for the purity of their water.

Children are at greatest risk from lead exposure, and school is where they spend much of their early lives. But cash-starved school administrators may see a choice between spending money on teachers or on plumbing as no choice at all.

"They feel it's almost better not to sample, because you're better off not knowing," Marc Edwards, a Virginia Tech University civil engineering professor who

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A student in Flint, Mich., had her blood tested in January.

- Lead is a neural toxin
  - Especially serious in children
- EPA: Pb & Cu Rule Published in 1991
  - If **lead** concentrations exceed an action level of **15 ppb** in more than 10% of customer taps sampled (i.e., 90%ile), the system must undertake a number of additional actions to control corrosion.

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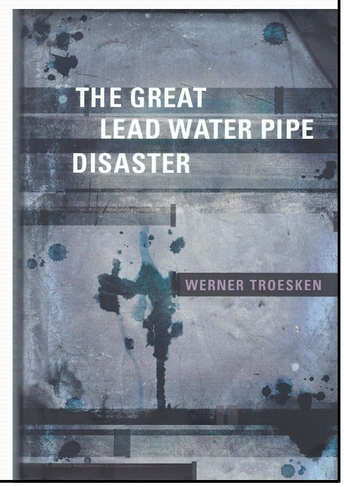
Public Outrage

- 2003 in DC & elsewhere

- The Great Lead Water Pipe Disaster
  - Werner Troesken
  - 2006 MIT Press



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Why did the DC crisis happen?

- Unintended consequences of decisions made to protect public health
- Need to provide clean water to cities
  - Disinfect with chlorine
  - Lead is a great piping material
- Some secondary problems that need fixing - carcinogens
  - Solution: Convert chlorine to chloramines?
  - Oops

First, a short history of municipal drinking water

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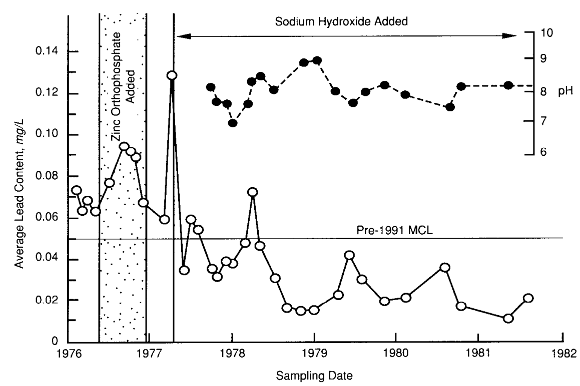
How to avoid Lead problems

- Optimized corrosion control treatment
  - Elevated pH and control of alkalinity
  - Addition of orthophosphate based corrosion inhibitors
- Other guidance
  - Keep oxidized environment
  - Keep chloride to sulfate ratio low
  - Minimize changes in distributed water chemistry
- Removal lead from system
  - Lead service lines
  - Lead in plumbing fixtures

Pb mitigation in Boston

- Karalekas study



Source: *Karalekas et al. (1983).*
Figure 4-2 Mean levels of lead in samples taken from Boston, Massachusetts, and Somerville, Massachusetts, 1976-1981

From: Internal Corrosion and Depositional Control, by Schock
Chapt. 17 in Water Quality and Treatment (5th ed), 1999

Pb Mitigation

- Impacts on other corrosion byproducts

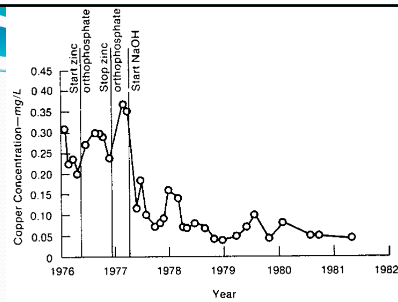


Figure 3. Mean levels of copper in samples taken from Boston and Somerville, Mass., 1976–1981

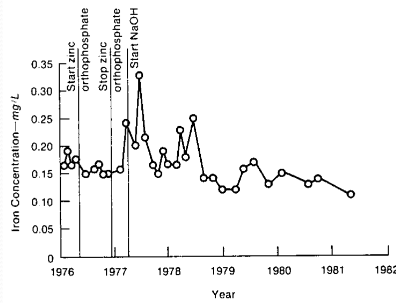


Figure 4. Mean levels of iron in samples taken from Boston and Somerville, Mass., 1976–1981

From: Karalekas et al., 1983 [J.AWWA 75:2:92]

Pb: Equations

- Redox
- Solubility

From: Aquatic Chemistry Concepts, by Pankow, 1991

- Mass Balance

$PbO_{2(s)} + 4H^+ + 2e^- = 2H_2O + Pb^{2+}$	$\log K = 49.2$
$Pb^{2+} + 2e^- = Pb_{(s)}$	$\log K = -4.26$
$PbO_{(s)} + 2H^+ = Pb^{2+} + H_2O$	$\log\ {}^*K_{s0} = 12.7$
$Pb^{2+} + H_2O = PbOH^+ + H^+$	$\log\ {}^*K_1 = -7.7$
$PbOH^+ + H_2O = Pb(OH)_2^o + H^+$	$\log\ {}^*K_2 = -9.4$
$Pb(OH)_2^o + H_2O = Pb(OH)_3^- + H^+$	$\log\ {}^*K_3 = -11.0.$

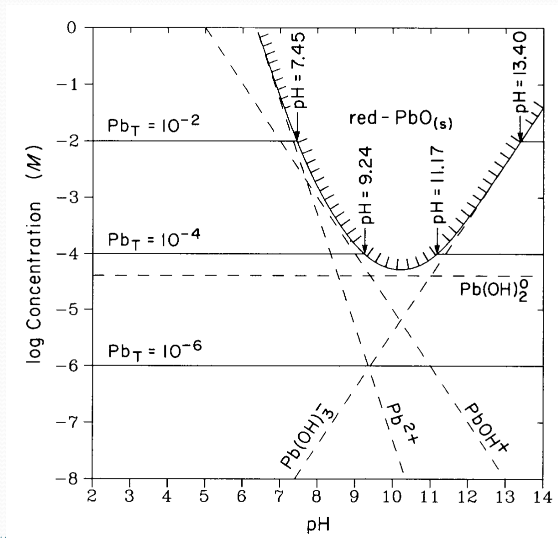
$$Pb_T = [Pb^{+2}] + [PbOH^+] + [Pb(OH)_2^0] + [Pb(OH)_3^-]$$

$$= [Pb^{+2}]\left(1 + \frac{{}^*K_1}{[H^+]} + \frac{{}^*K_1{}^*K_2}{[H^+]^2} + \frac{{}^*K_1{}^*K_2{}^*K_3}{[H^+]^3}\right)$$

$$Pb_T = {}^*K_{so}[H^+]^2\left(1 + \frac{{}^*K_1}{[H^+]} + \frac{{}^*K_1{}^*K_2}{[H^+]^2} + \frac{{}^*K_1{}^*K_2{}^*K_3}{[H^+]^3}\right)$$

Pb (+II): Solubility

- Red- PbO(s)



From: Aquatic Chemistry Concepts, by Pankow, 1991

Pb: Predominance Equations I

- Again, in general

$$Pb_T = {}^*K_{so}[H^+]^2\left(1+\frac{{}^*K_1}{[H^+]}+\frac{{}^*K_1{}^*K_2}{[H^+]^2}+\frac{{}^*K_1{}^*K_2{}^*K_3}{[H^+]^3}\right)$$

- Which can reduce to (depending on predominance):
  - For Pb^{+2}

$$Pb_T \approx {}^*K_{so}[H^+]^2(1) = 10^{-12.7}[H^+]^2$$

  - For $Pb(OH)_2^o$

$$Pb_T \approx {}^*K_{so}[H^+]^2\left(\frac{{}^*K_1}{[H^+]}\right) = {}^*K_{so}{}^*K_1[H^+] = 10^{-20.4}[H^+]$$

  - For $Pb(OH)_2^o$

$$Pb_T \approx {}^*K_{so}[H^+]^2\left(\frac{{}^*K_1{}^*K_2}{[H^+]^2}\right) = {}^*K_{so}{}^*K_1{}^*K_2 = 10^{-29.8}$$

Oxidation Chemistry of Pb

- Oxidation States
  - o, +II, +IV
- Solubility
  - o oxidation state: insoluble
    - Pb(s)
  - +II oxidation state: relatively soluble
    - PbO(s) (red & yellow), $Pb(OH)_2(s)$
  - +IV oxidation state: essentially insoluble
    - $PbO_2(s)$

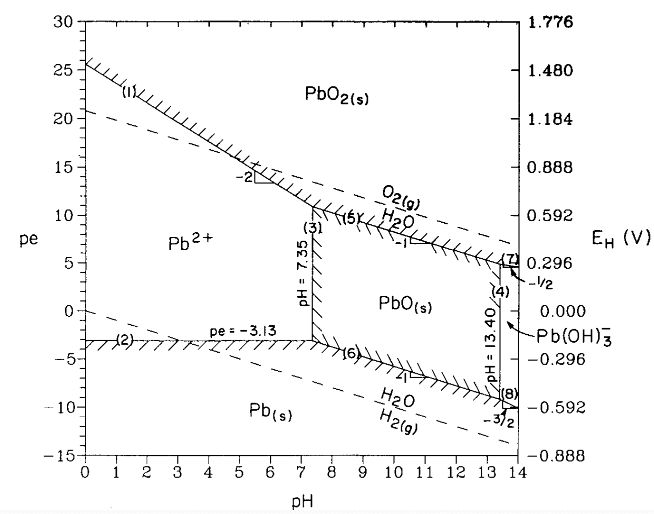
Pb: Predominance Equations II

$2pe = 49.2 + \cancel{\log\{PbO_{2(s)}\}} - \boxed{\log\{Pb^{2+}\}} - 2\cancel{\log\{H_2O\}} - 4pH$	(21.12)	$\frac{PbO_{2(s)}}{Pb^{2+}}$
$-\boxed{\log\{Pb^{2+}\}} + \cancel{\log\{H_2O\}} = 12.7 - 2pH + \cancel{\log\{PbO_{(s)}\}}$	(21.16)	$\frac{PbO_{(s)}}{Pb^{2+}}$
$2pe = 36.5 - 2pH + \cancel{\log\{PbO_{2(s)}\}} - \cancel{\log\{PbO_{(s)}\}} - \cancel{\log\{H_2O\}}$	(21.17)	$\frac{PbO_{2(s)}}{PbO_{(s)}}$
$2pe = -4.26 + \boxed{\log\{Pb^{2+}\}} - \cancel{\log\{Pb_{(s)}\}}$	(21.14)	$\frac{Pb^{2+}}{Pb_{(s)}}$
$+\boxed{\log\{Pb^{2+}\}} + \cancel{\log\{H_2O\}} = 12.7 - 2pH + \cancel{\log\{PbO_{(s)}\}}$	(21.16)	$\frac{PbO_{(s)}}{Pb^{2+}}$
$2pe + \cancel{\log\{H_2O\}} = 8.44 - 2pH + \cancel{\log\{PbO_{(s)}\}} - \cancel{\log\{Pb_{(s)}\}}$	(21.19)	$\frac{PbO_{(s)}}{Pb_{(s)}}$

From: Aquatic Chemistry Concepts, by Pankow, 1991

Pb Predominance

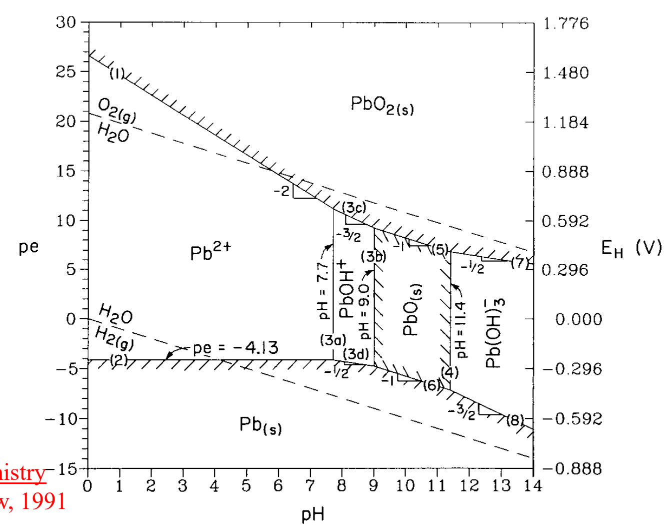
- $Pb_T = 10^{-2}$ M



From: Aquatic Chemistry Concepts, by Pankow, 1991 (pg. 468)

Pb Predominance

- $Pb_T = 10^{-4}$ M



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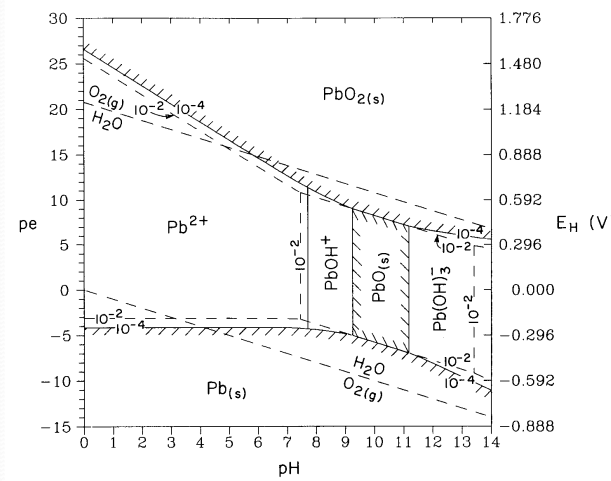
Pb Predominance

- Combined



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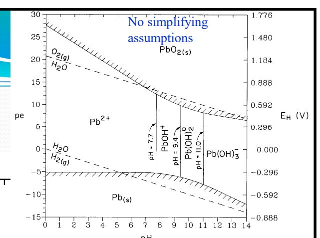
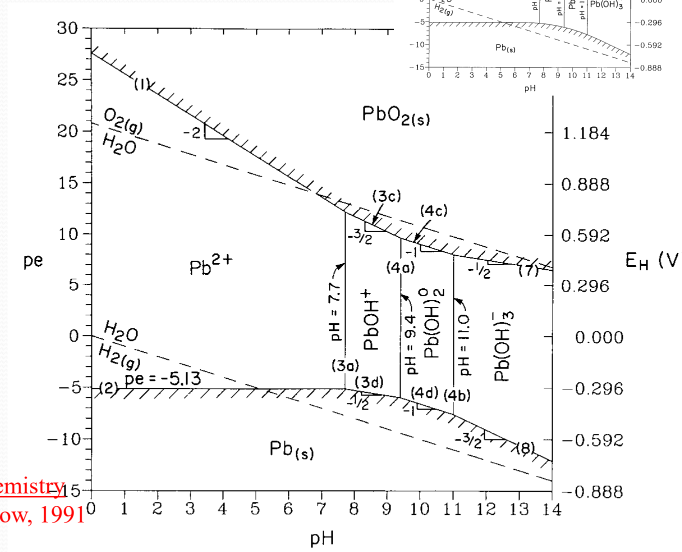
Pb Predominance

- $Pb_T = 10^{-6}$ M





From: Aquatic Chemistry Concepts, by Pankow, 1991 (pg. 467)

- To next lecture

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