Part 1: Use of Desktop Studies to Understand Corrosion Control and Metal Release

Confluence Engineering Group LLC
Danbi Won, Virpi Salo-Zieman, Alex Mofidi, Melinda Friedman

2019 PNWS-AWWA

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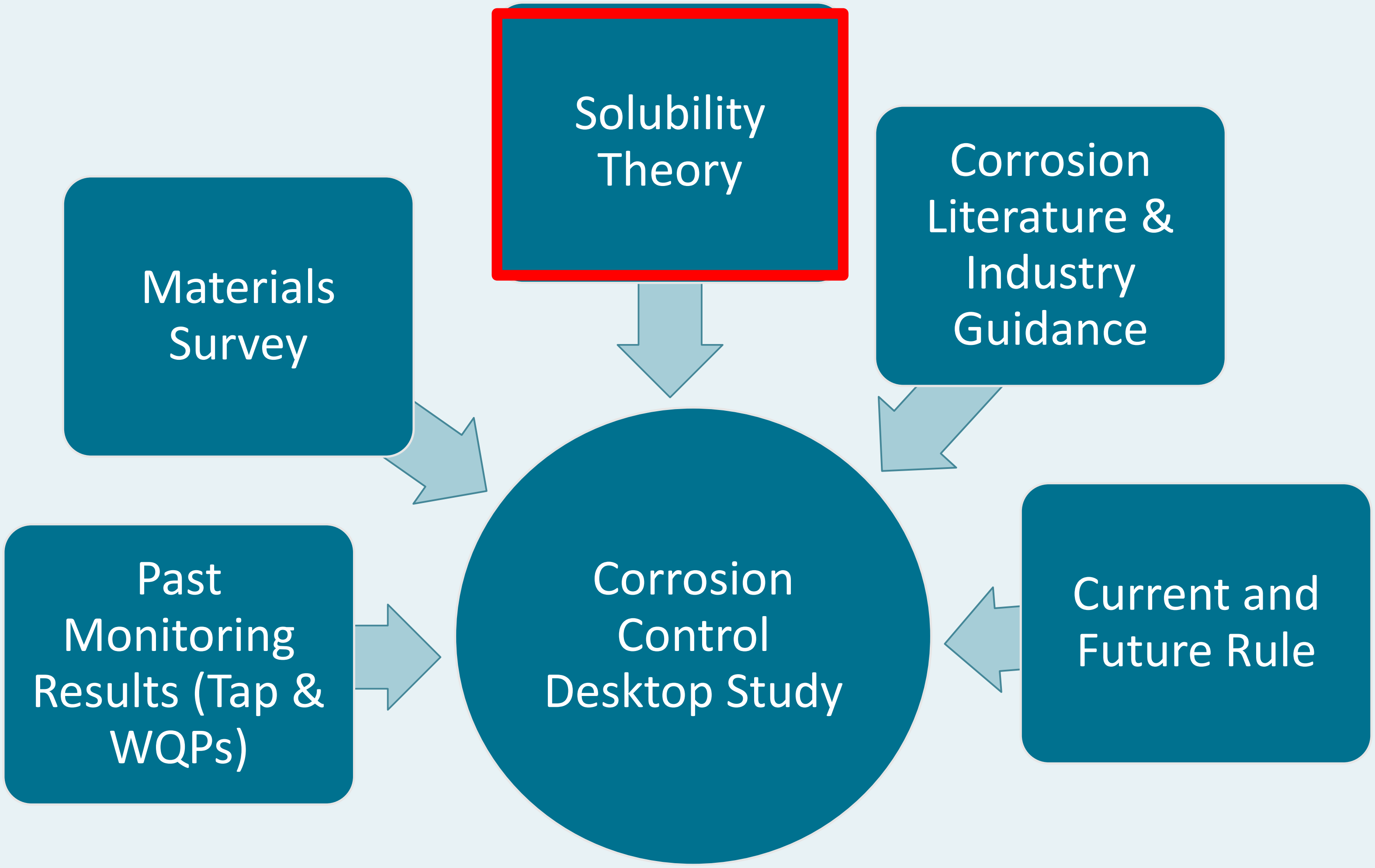
A RIVER RUNS THROUGH IT
2019 PNWS-AWWA CONFERENCE
VANCOUVER, WASHINGTON

Agenda

1. Desk-Top studies and role of chemistry models
2. Key model inputs
3. Use of spreadsheet and modeling tools
4. Case study – Tacoma Water
5. Conclusions and recommendations

Corrosion Control Evaluation – Desk-Top Approach

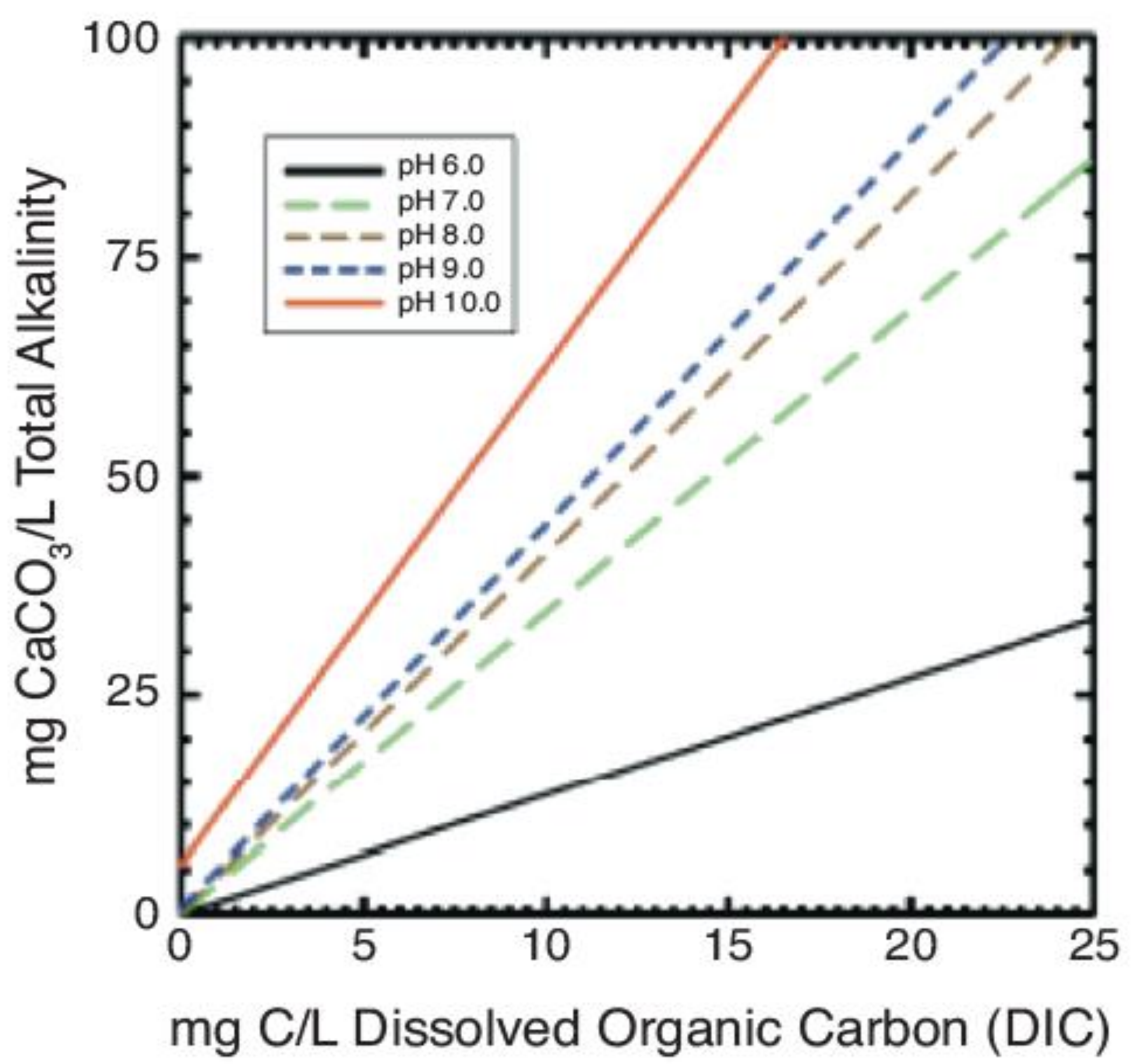


Dissolved Inorganic Carbon (DIC) is a Critical CCT Parameter

$DIC = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

Impacts Metals Solubility and Speciation

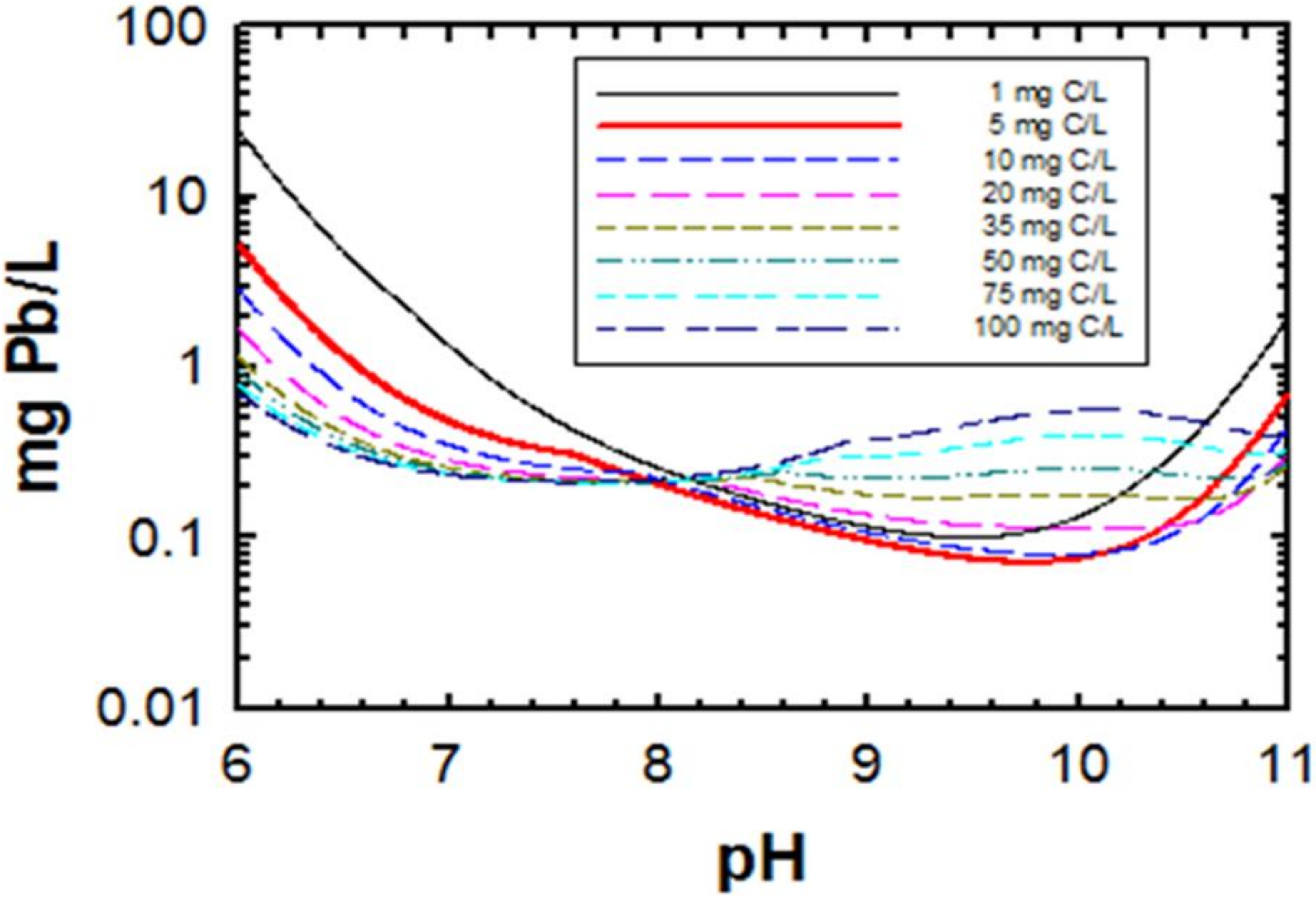
Impacts Buffer Intensity of Water



Source: Schock et al. 2014a

Lead (II) Solubility

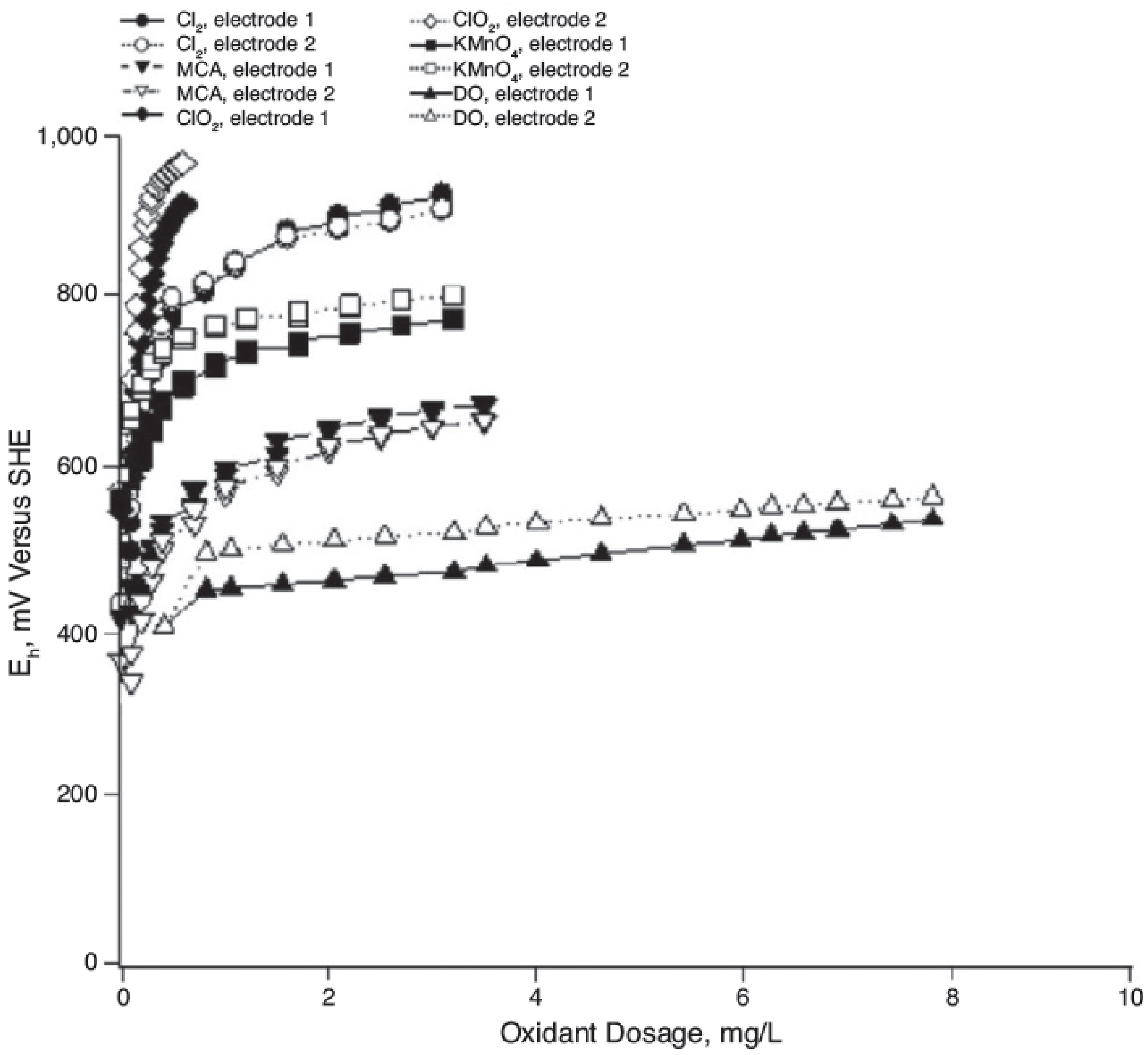
- Classic Pb (II) solubility curve Versus pH
  - As a function of DIC



Source: Schock 2018 – AWWA Corrosion 101 Webinar

Eh ~ Oxidation-Reduction Potential (ORP)

- Tendency of a species to lose or gain an electron, and therefore become oxidized or reduced
- Typically controlled by disinfectant residual concentration in drinking water systems



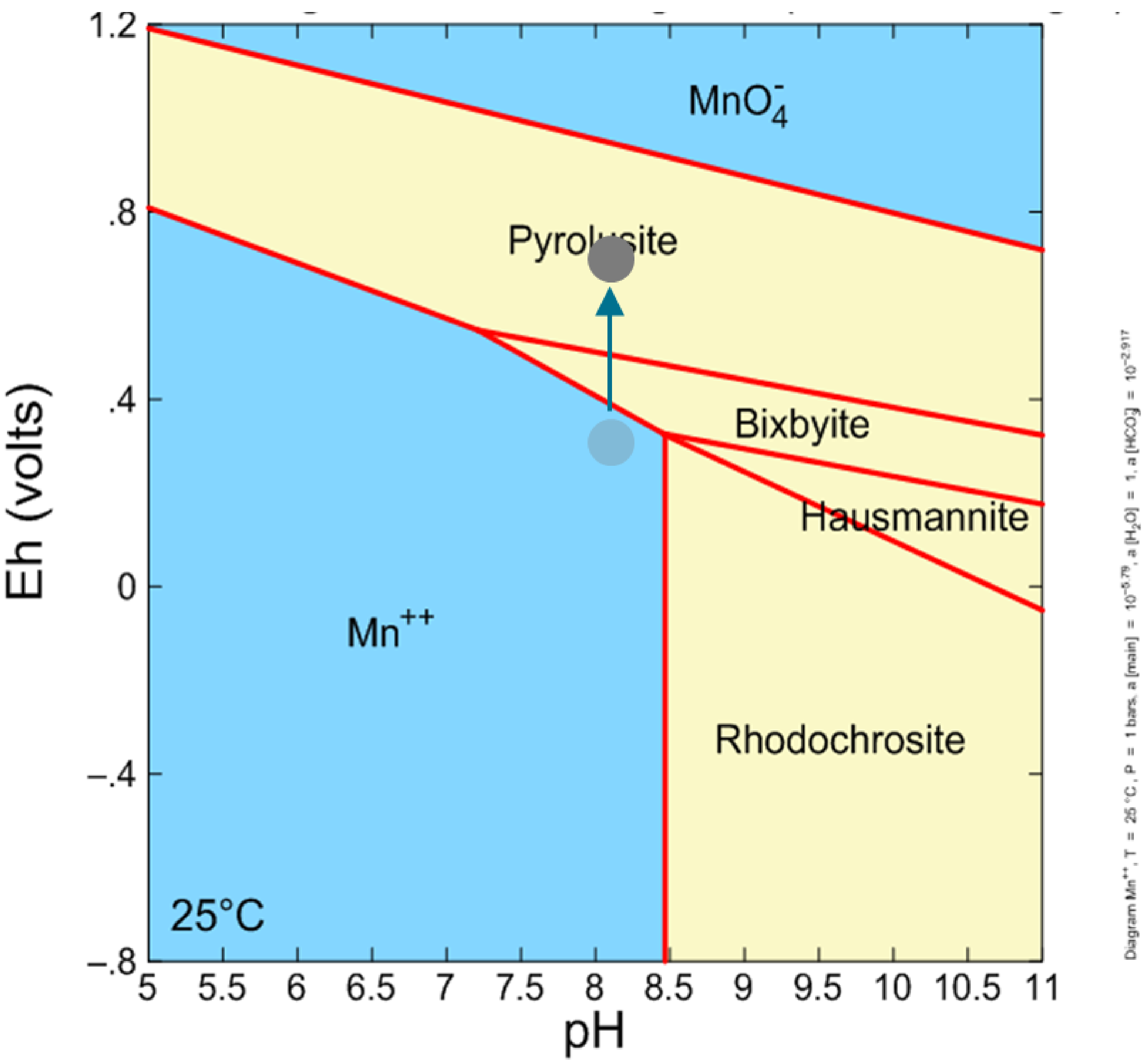
Cl_2—chlorine, ClO_2—chlorine dioxide, DO—dissolved oxygen, Eh—half-reaction electrode potential (measured in millivolts), $KMnO_4$—potassium permanganate, MCA—monochloramine, SHE—standard hydrogen electrode

Dissolved inorganic carbon = 5 mg/L C; pH = 8; temperature = 23°C

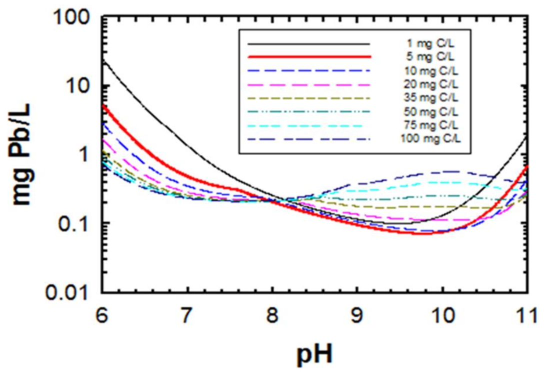
Copeland and Lytle 2014

Pourbaix Diagram

- Eh-pH diagram
- Example for Manganese
  - Mn=0.1 mg/L
  - DIC = 15 mg C/L



Use of Spreadsheet and Modeling Tools



Purpose: construction of system-specific metal curves

Chemistry

Metal

Solubility ↓, Scale Stability ↑

pH

DIC

Temperature

Ca, SO4, Cl, TDS

Pb, Cu, Fe, Mn

Goals: 1. Demonstrate that changes to water chemistry are moving in the right direction!
2. Select right CCT chemicals and end-point.

Spreadsheet Tool 1. Water!Pro

Corrosivity of
1) current condition
2) after blending different water
3) after chemical addition

Disclaimer | **MAIN MENU** | Overview

Water!Pro ™
Treating Drinking Water
Version 6.50

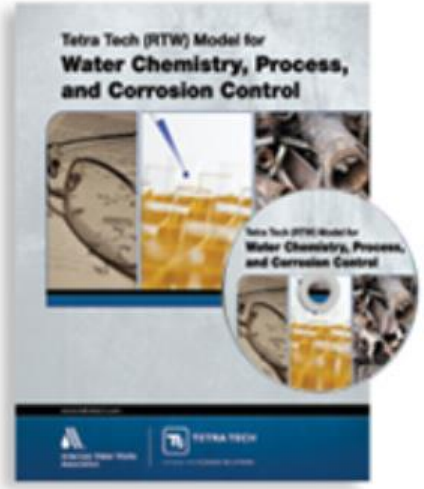
WaterPro	For modeling coagulation, corrosion control, disinfection, and other chemical processes. This worksheet is the main modeling program.
WP-Results	Summary of water characteristics, chemical addition and chemical and operational cost from worksheet "WaterPro."
WP-Cost Input	Entry for chemical purchase cost, sludge characteristics and relative operating cost for water treatment.
WP-Input-Storage	Worksheet for storing and retrieving up to 100 sets of inputted data from WaterPro worksheet. Data is saved and retrieved from this worksheet via the WaterPro worksheet. Data input may also be saved into this worksheet manually.
Corrosion Modeling	Corrosion control program for modeling & plotting chemical dosages, alkalinity, pH, lead & copper, buffer intensity, aggressive, Langelier, CCPP & Ryznar indices.
Indices &	Worksheet for calculating corrosion indices and corrosion chemical treatment for up to 500 sets of data water quality inputs.
Pb & Cu Guidance	Guidance worksheet to assist water systems with selecting effective treatment strategies for controlling lead and copper in drinking water.
Buffer Intensity	Plots buffer intensity (mMol/pH) versus pH. It is the water's resistance to changes in pH. Also plots CCPP versus pH.
Limestone Contactor	To assist the user in design of limestone filters for water systems installing corrosion control. Has CO_2 pre-treatment option for waters with low buffering capacity and high pH.
Limestone Target	Carbon dioxide dosage is determined based on desired treated water calcium concentration and targeted Langelier Saturation Index for designing limestone contactors.
SAR	Sodium adsorption ratio model. Both simple and rigorous methods are used. SAR calculations for irrigation, rhizosphere root zone and drainage waters.
Blend	For modeling blend of two source waters. Blended results can then be automatically inputted into worksheets WaterPro and CorrosionGraphs for further evaluation.
BlendingPro	For modeling the blend up to six source waters. Blended results can then be automatically inputted into worksheets WaterPro and CorrosionGraphs for further evaluation.
Water Soft 1	Water Softening (Lime/Soda Ash) - Selective Calcium Process.

Main_Menu | WaterPro | WP-Results | WP-CostInput | WP-Input-Storage | CorrosionModeling | BufferIntensity | Indices | Pb & Cu Decision Guidance | Limestone Contactor | LimestoneTarget | SAR | Blend

Schott Software LLC

Giardia Log Inact (Cl_2)	This program calculates the log inactivation ... for various pH, temperature, working volume ...
Cyanotoxins	This program calculates the log and % oxidation of micro... on free chlorine residual for various pH, temperature, working volume ...
ChemDose ChemDose(PS)	Worksheet for calculating chemical solution strength, specific gravity of solution mix, and chemical dosages. There are two worksheets - one for entering chemical feed rate and the other for entering chemical pumping settings (stroke/speed).
Jar Testing	This worksheet is designed to assist in the makeup of stock solution for jar testing and calculate delivered volume for individual jar dosages.
TTHMs, HAAs & CH	For modeling precursors (THMs, HAA6 & CH) in raw water and distribution system.
Br & O_3	Predictive models for bromate formation with & without ammonia and predictive model for ozone decay.
Ar(V)	A simplified isotherm equation predicts arsenate removal using iron coagulant ($FeCl_3$). Model predicts arsenate removal to within +/- 13 percent (90% confidence) at pH 6.5-8.
IronMang	To determine stoichiometry oxidation for iron and manganese using chlorine, ozone oxygen, chlorine dioxide, and potassium permanganate.
AnCatBal	The mass/volume (mg/L) of anions and cations entered into this worksheet are summed and the totals compared.
LabSheet	Results from the AnCatBal worksheet are automatically entered into this professional form for printout.
Metal Solids	Worksheet that displays theoretical lead, copper and zinc solubility concentrations for each metal before and after chemical treatment based on data entry in "WaterPro."
ICA	Worksheet that summarizes percent concentrations of ions and ion pairs, pHs, solubility constants, and activities.
Pb Diagram	Chart that displays a two-dimensional solubility diagram for lead related to the characteristics calculated in STEP 4 of "WaterPro."
Pb Contour	Chart that displays the contour diagram for lead solids.
3D Pb, DIC & pH	Chart that displays a three-dimensional solubility diagram for lead. Plotted are Pb, DIC & pH.
Al Diagram	A plot of the "Solubility Diagram for Amorphous Aluminum Hydroxide."
Definitions & Settings	Defines relative terms used in this program.
References	A list of references used to develop this program.

Spreadsheet Tool 2. Tetra Tech (RTW) Model



Tetra Tech (RTW) Model for Water Chemistry, Process, and Corrosion Control

Manual

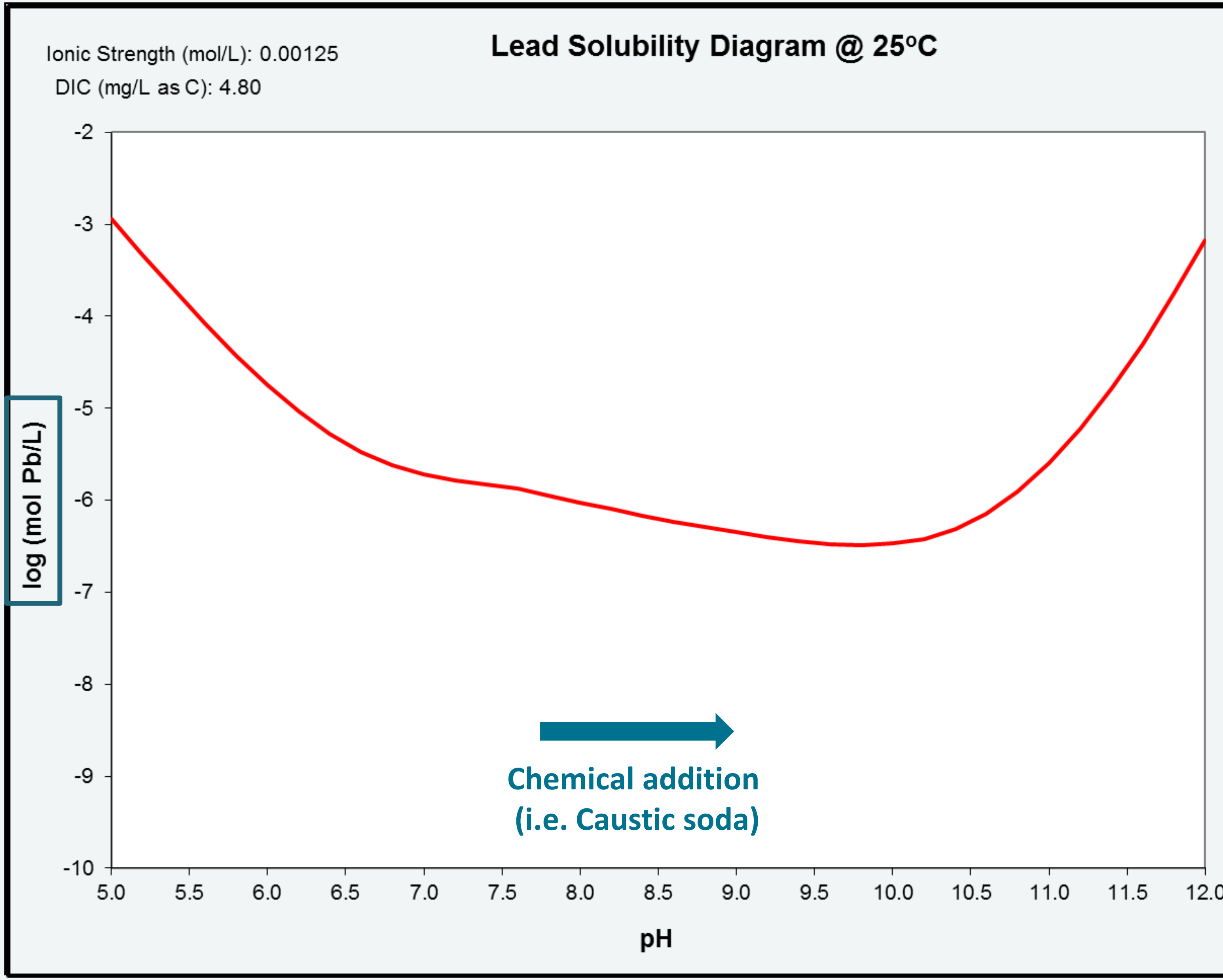
Corrosion Model	Calculates the interim & treated water characteristics, where the initial water quality data & the amount of chemicals to be added for treatment are entered.
Blending Water Model	Calculates the interim & treated water characteristics, having initial waters' (2 sources) quality data & the chemical dosages to be added for water treatment.
Coagulant Dosage Calculations	Determines the coagulant volume required for jar testing & full-scale implementation, and estimates the dry weight of the produced sludge.
Oxidant Dosage Calculations	Determines oxidant dosages for oxidizing iron, manganese, arsenic, and/or sulfide & calculates the equivalent dosages of different oxidants
Sodium Hypochlorite Dosage Calculations	Calculates the volume of NaOCl to add for water treatment given peak and average flow rates and required NaOCl dosages.

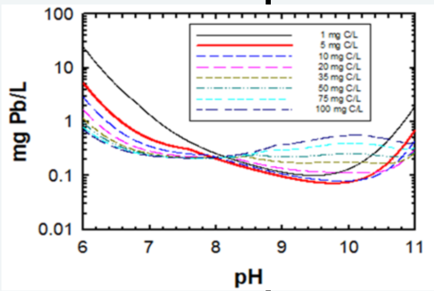
Other tools available, too!

Now, let’s look at examples.

Surface Water with Low Alkalinity (20 mg/L CaCO3) and DIC (4.8 mg/L C)

- Theoretical total metal release trends as function of pH
- Predict solubility trends, not actual concentrations measured in the fields
- Models are over-predicted concentration due to assumptions.
  - Pure lead
  - Infinite contact time
  - Equilibrium reached
  - at 25°C
- Predict approximate stability domains of different lead species based on DIC concentration and pH in water.
- Cerussite is dominant up to pH 7.6 in low alkalinity (low DIC) surface water.

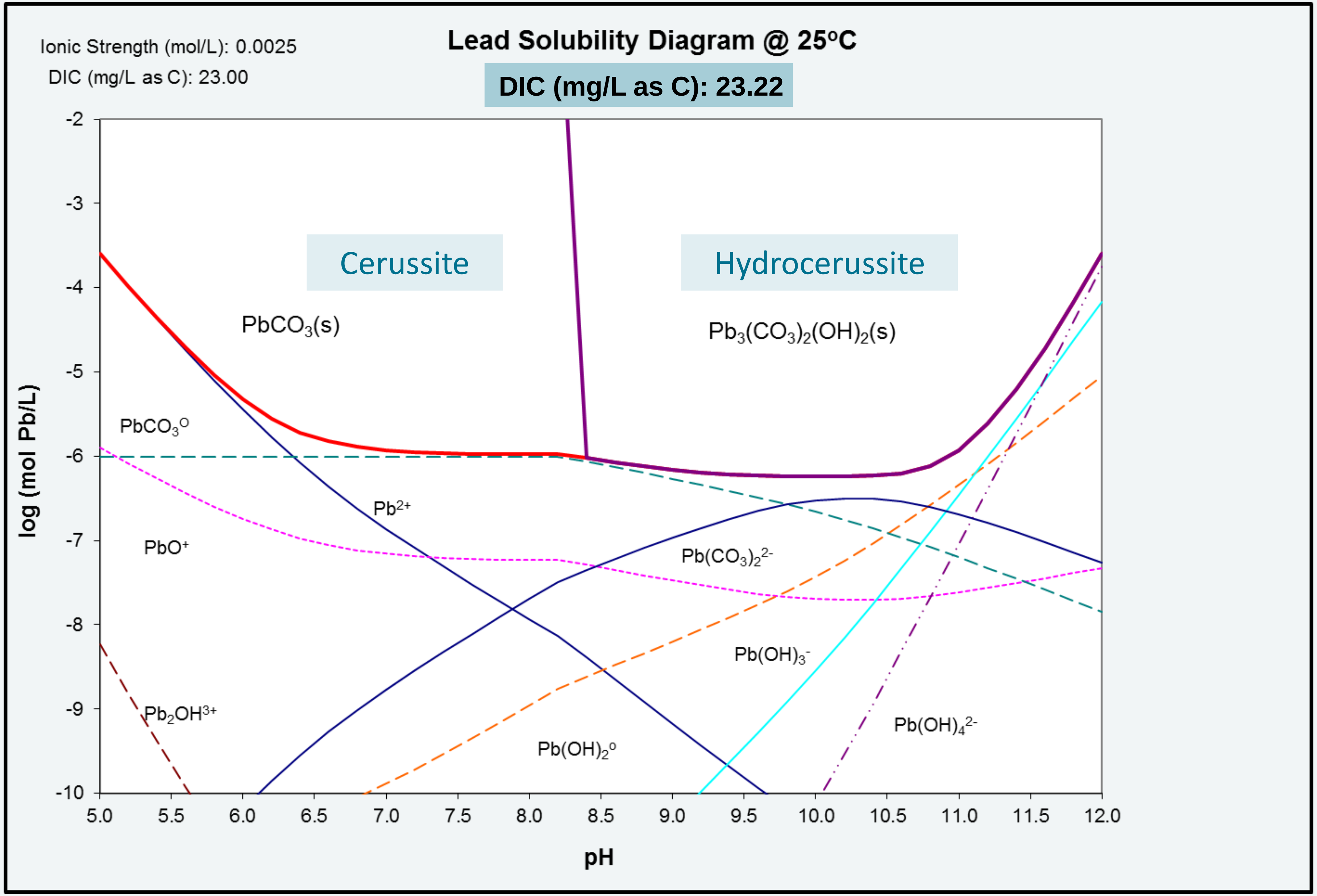




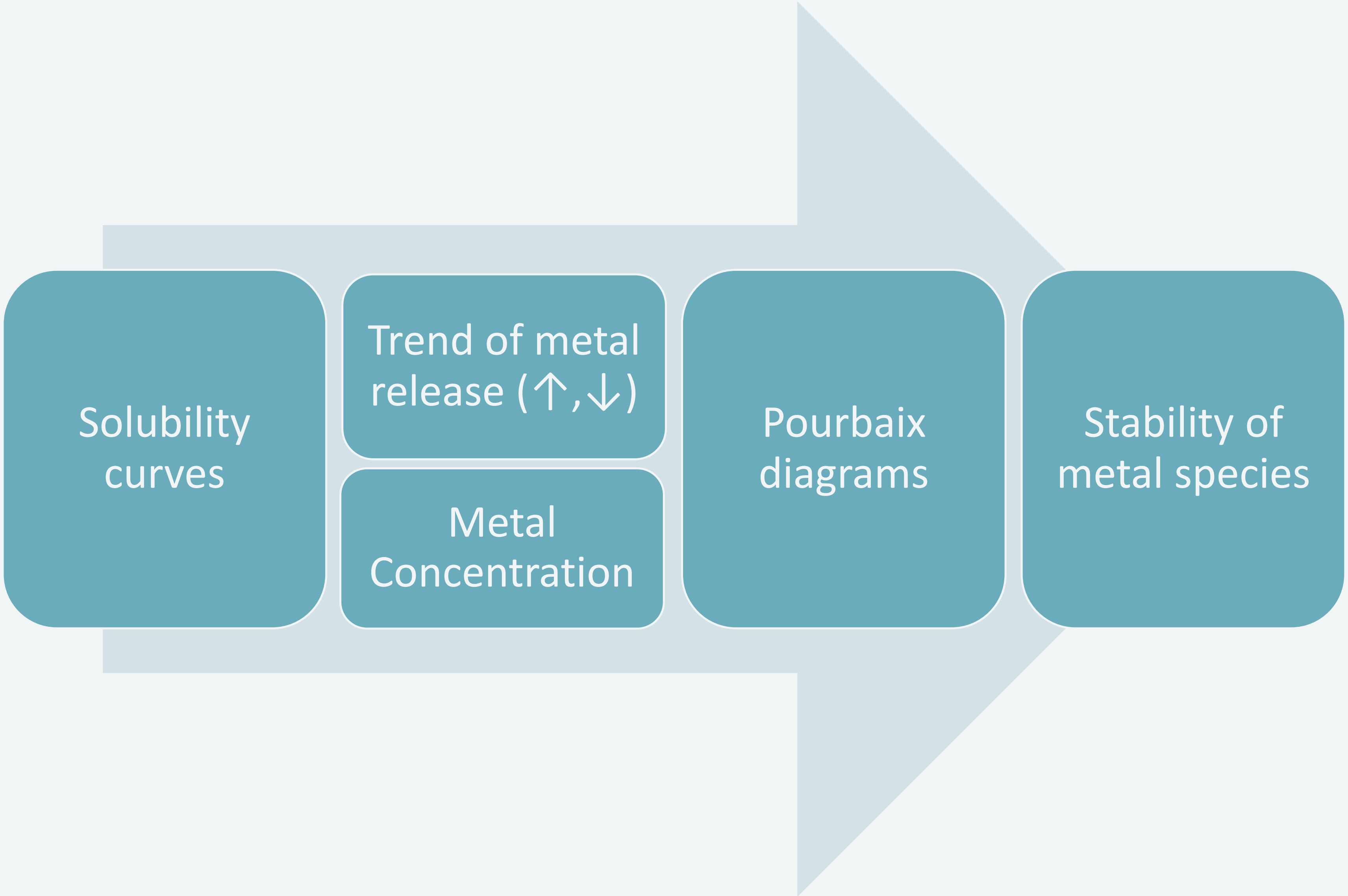
Groundwater with High Alkalinity (100 mg/L CaCO3) and DIC (23 mg/L C)

- Cerussite is dominant up to pH 8.4 in high alkalinity (high DIC) groundwater.
- Boundary shifts to right.
- We want to know how **stable** the species are.
- Why do we care?

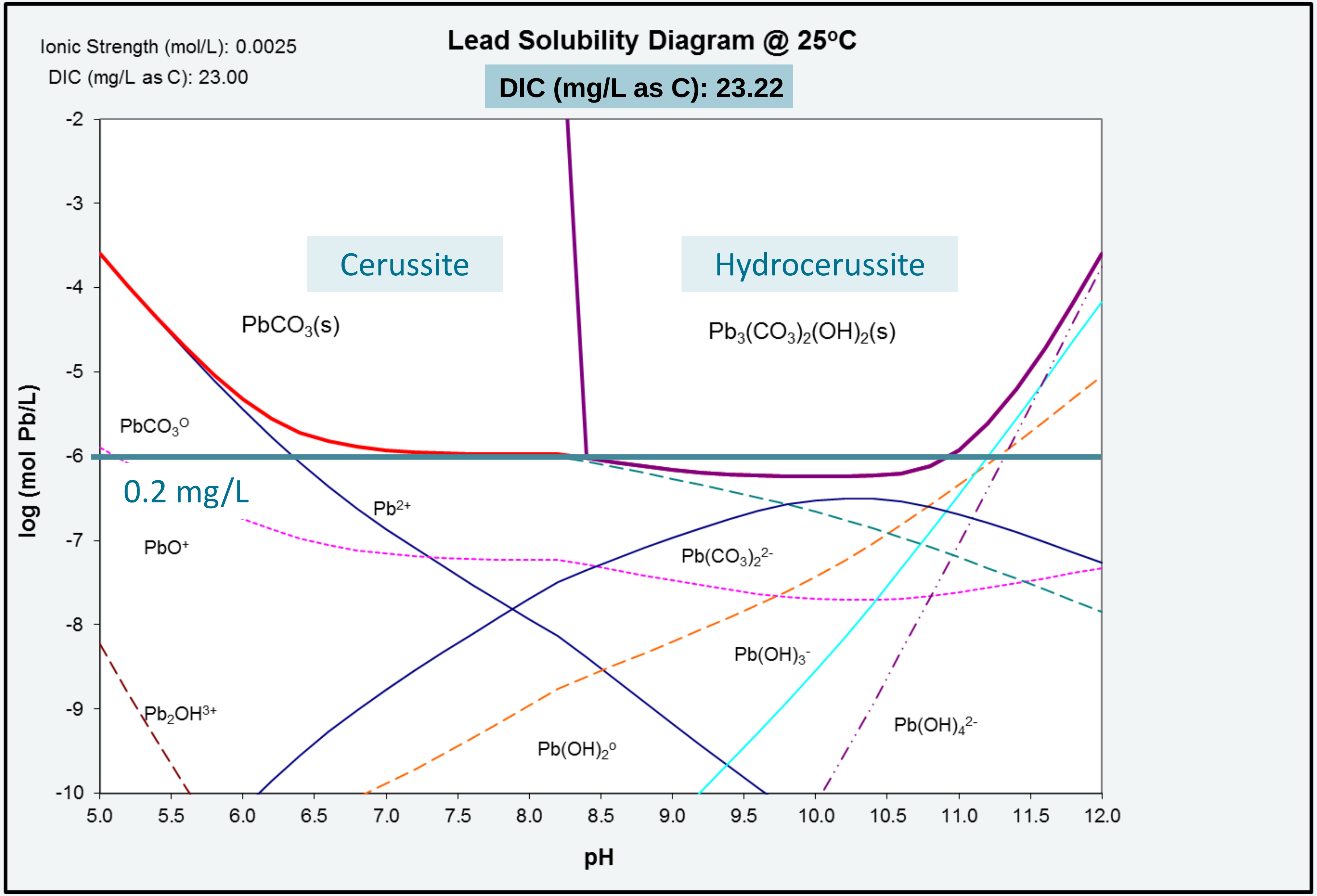
  \- We don't want to change the dominant species because that can increase particulate and soluble lead concentration.



Solubility model and Pourbaix diagrams



High lead concentration (0.2 mg/L) might represent lead service line.



Schematic relationship between solubility curves and pourbaix diagrams

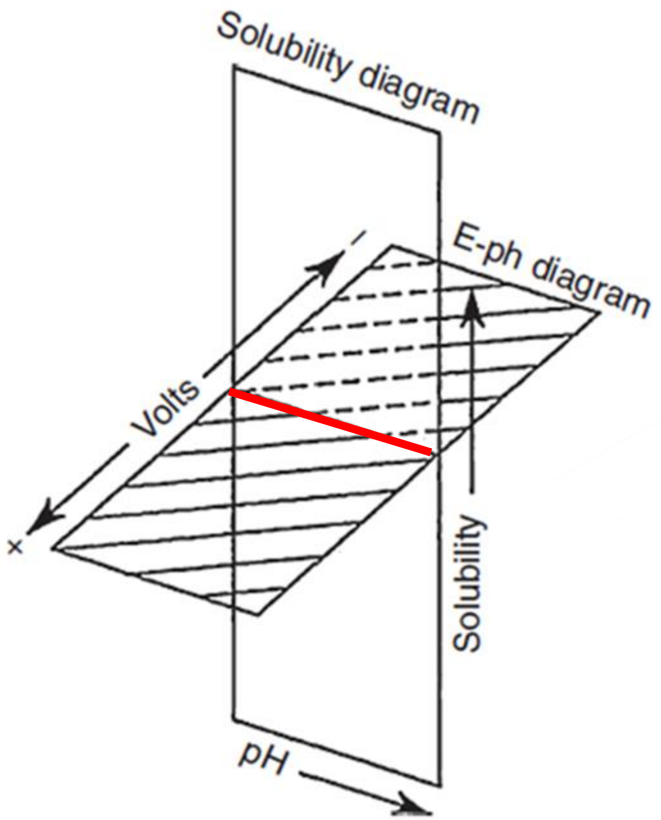
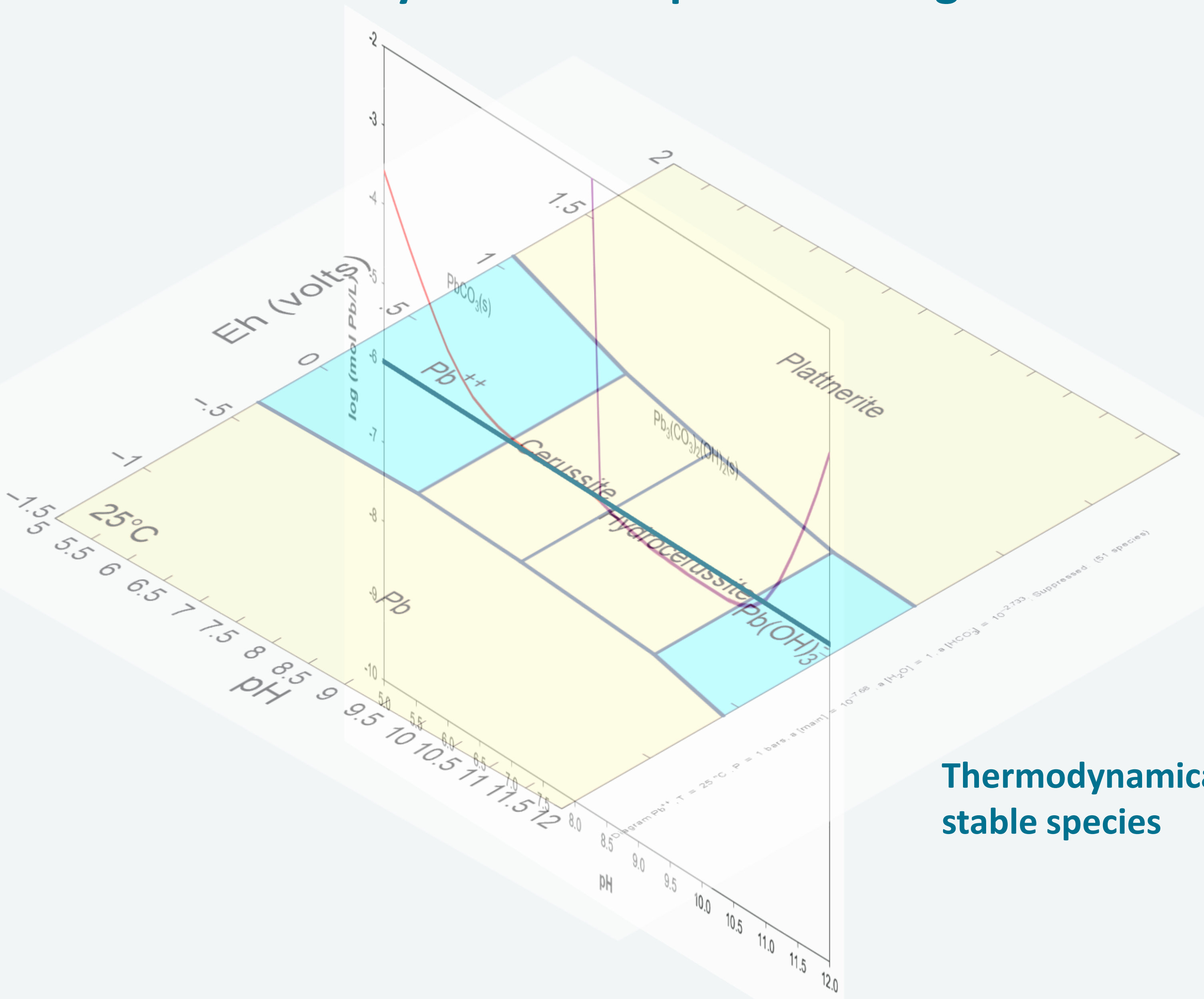


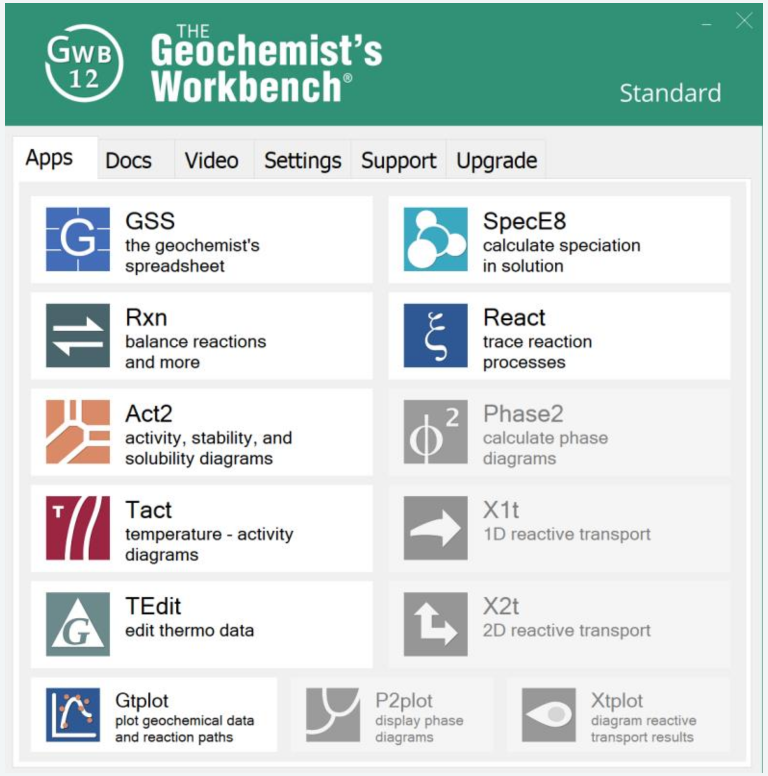
FIGURE 20-6 Schematic relationship between potential pH and conventional solubility versus pH diagrams.

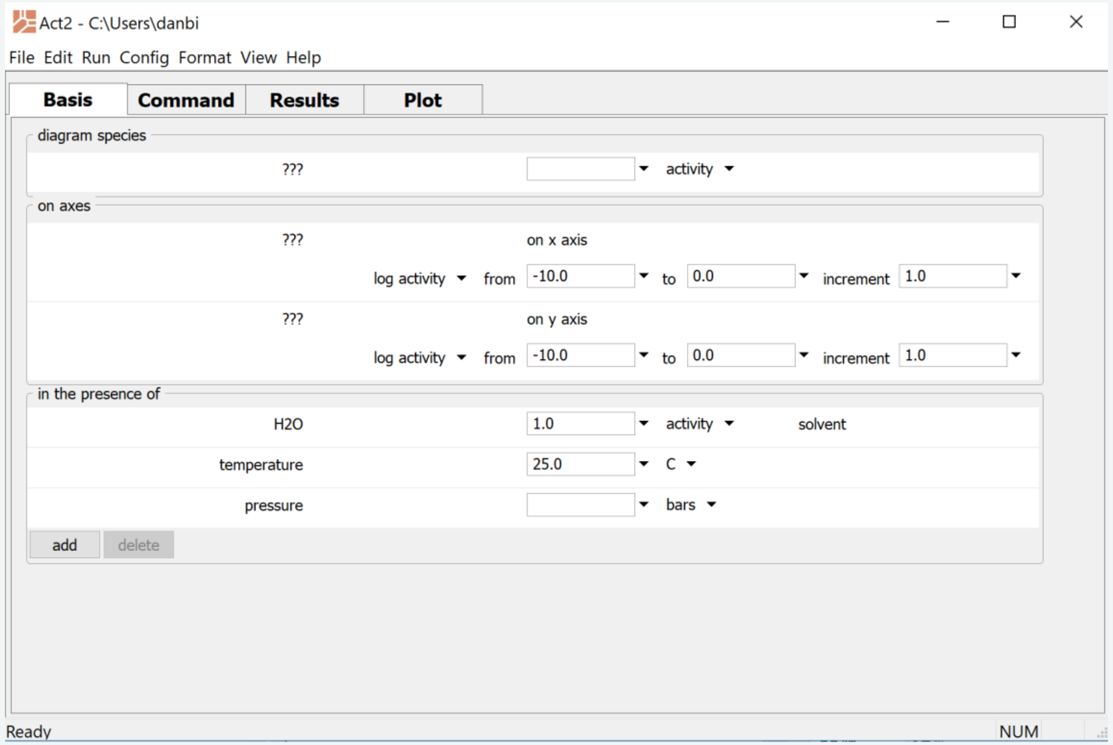
Shock and Lytle, Water Quality & Treatment, 6th Edition, 2011



Thermodynamically stable species

Slice solubility diagram at specific Pb concentration and **create** pourbaix diagram for that DIC. (0.2 mg-Pb/L and 23mg/L as C)





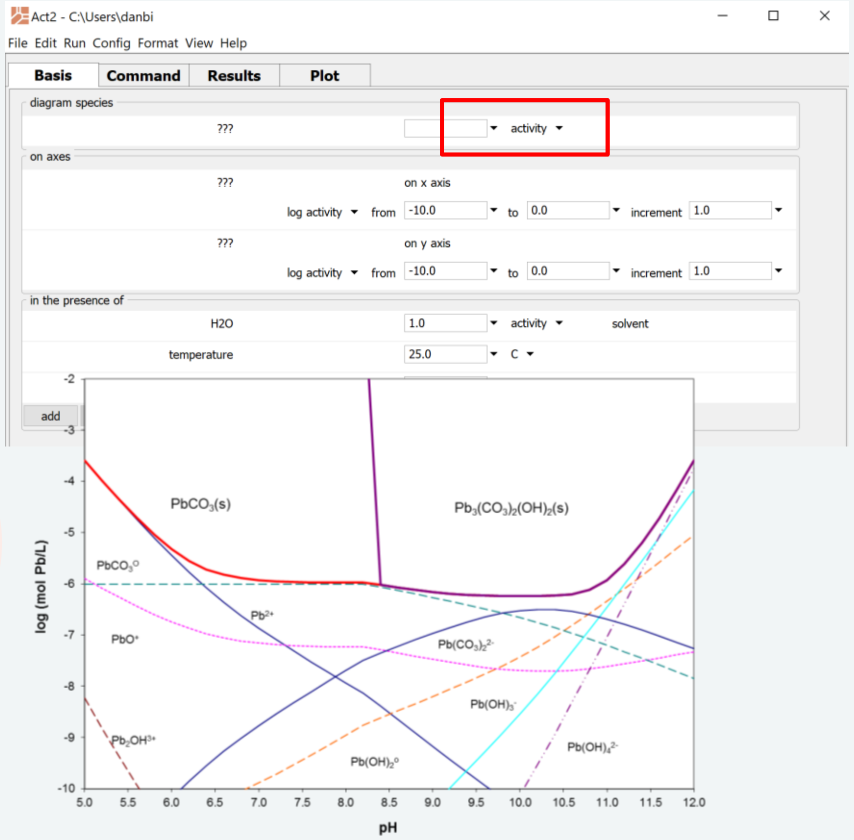
The Geochemist's Workbench

:create Pourbaix diagrams

What you need to be aware of when using GWB

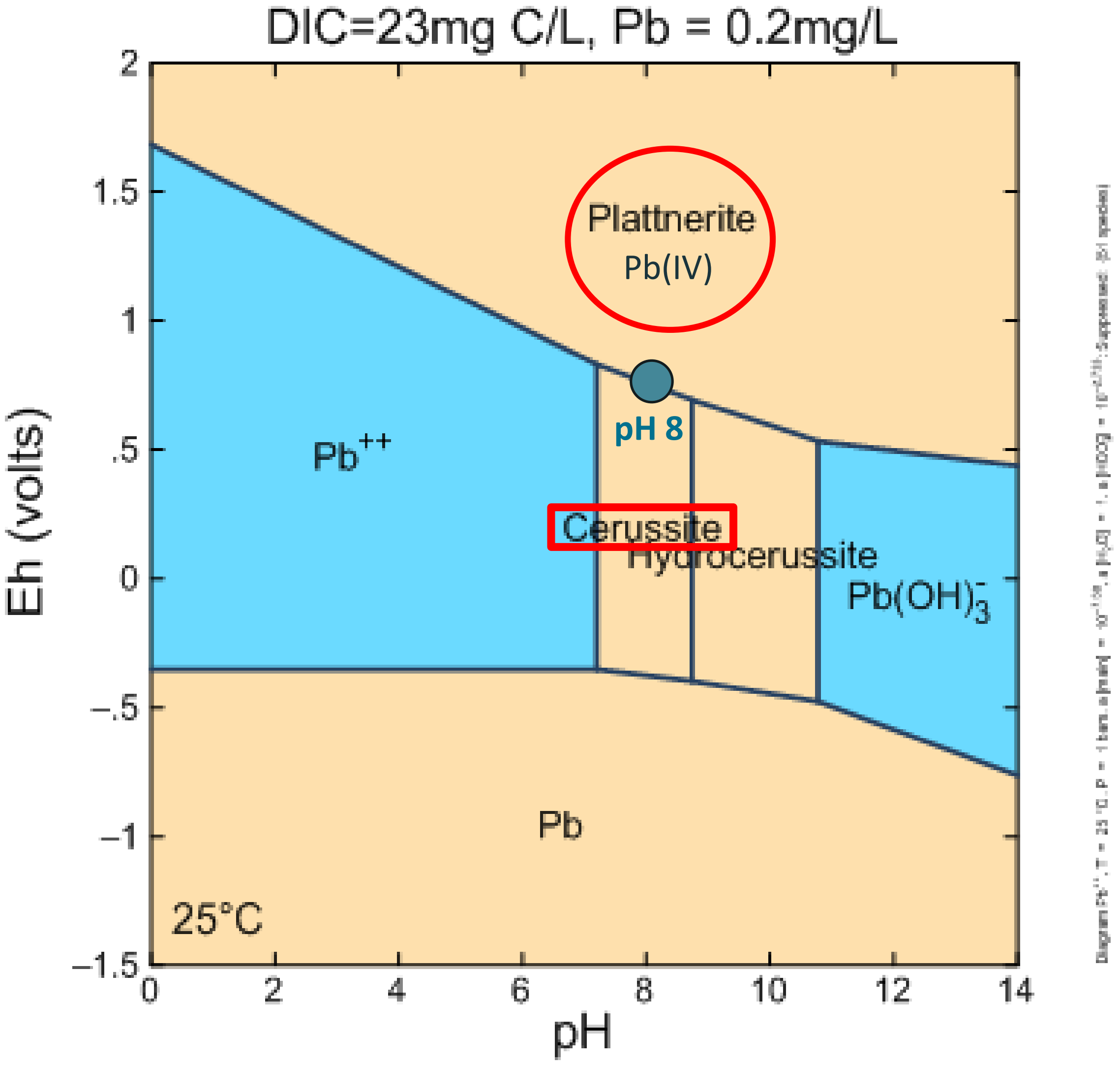
Complexity of model

- Thermodynamic data sets
- Activity coefficient models
- Suppress species

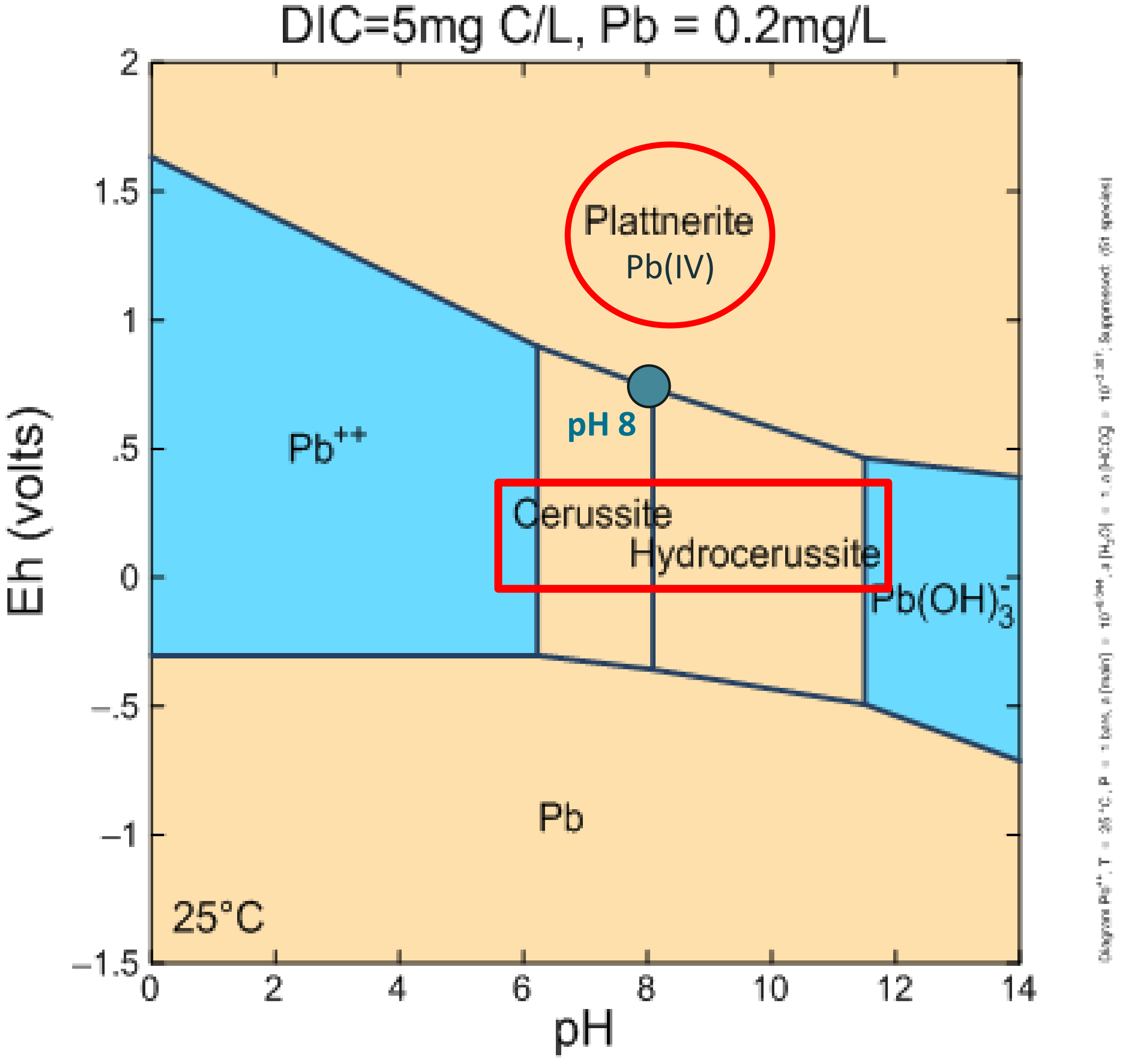


Pourbaix Diagram - Lead Speciation as a Function of ORP, DIC, and pH

Groundwater



Surface Water



Tacoma Water Corrosion Study

- Study Objectives – identify possible opportunities to further optimize lead levels
  - Considered optimized under LCR – 2016 90^{th} % = 2.1 ppb
  - Assess impacts of switching and blending surface water and groundwater
- Project Team
  - City of Tacoma (Tacoma Water)
  - HDR Engineering Inc.
  - Confluence Engineering Group, LLC
  - University of Washington, Seattle
  - ReiCorr Consulting

Water Quality Comparison Summary

Parameter	Surface Water	Groundwater
Free Chlorine (mg/L)	0.7 - 1.1	0.9 - 2.2
pH	8.1 - 8.2	7.4 - 7.8
Alkalinity (mg/L CaCO3)	20 - 27	42 - 98
DIC (mg/L C)	4 - 5	22 - 24
Conductivity (µs/cm)	29 - 45	58 - 125
Chloride (mg/L)	2 - 2.9	3.5 - 9.1
Sulfate (mg/L)	1.7 - 8.3	5.1 - 12.3

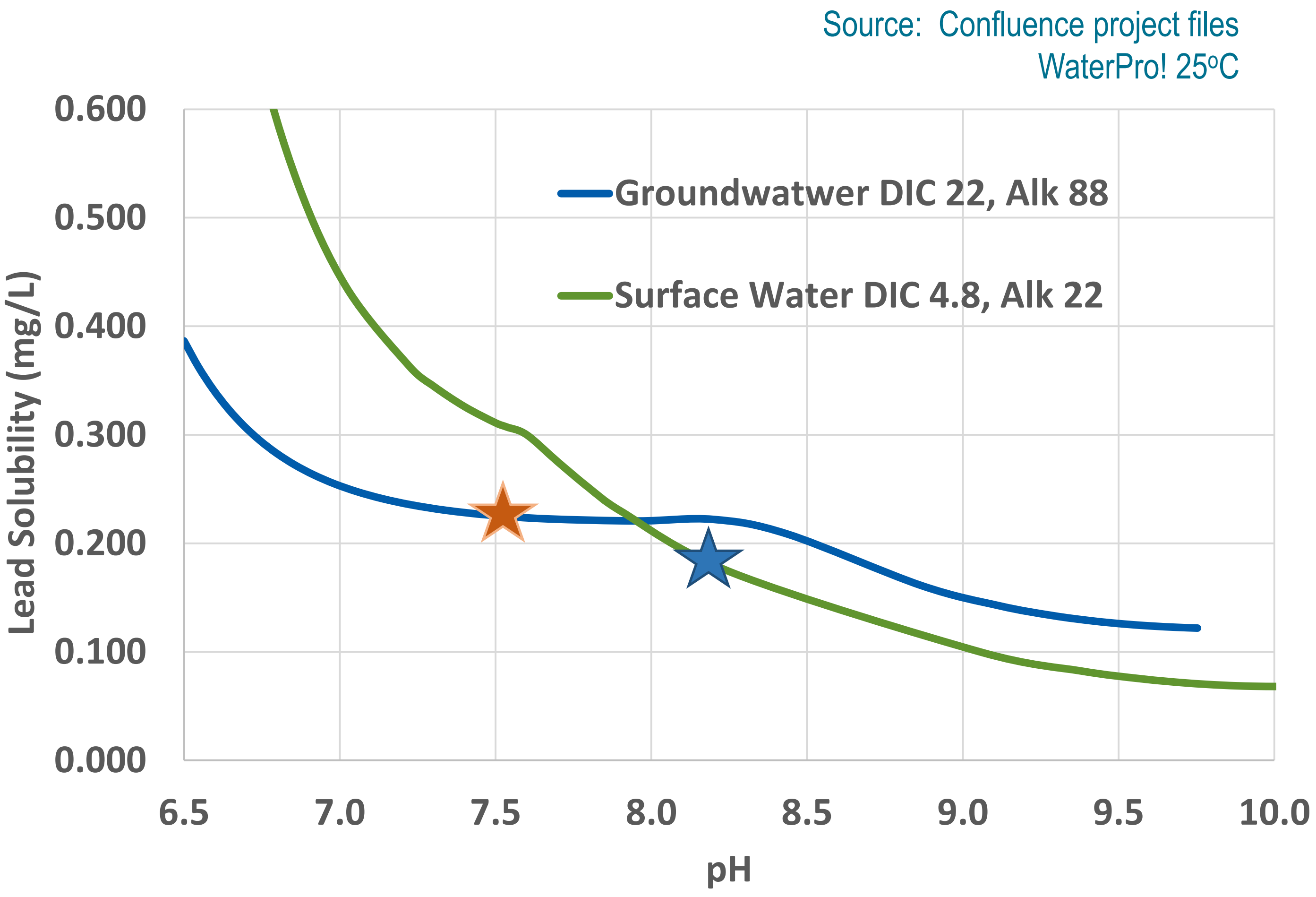
Source: Tacoma Water

Tacoma Water Pilot Rigs

- Materials
  - Brass meters
  - Copper pipe
  - Lead goosenecks
- Stage 1 – Surface Water
- Stage 2 – Groundwater
- Stage 3 – Surface Water
- Stage 4/5 - Blends

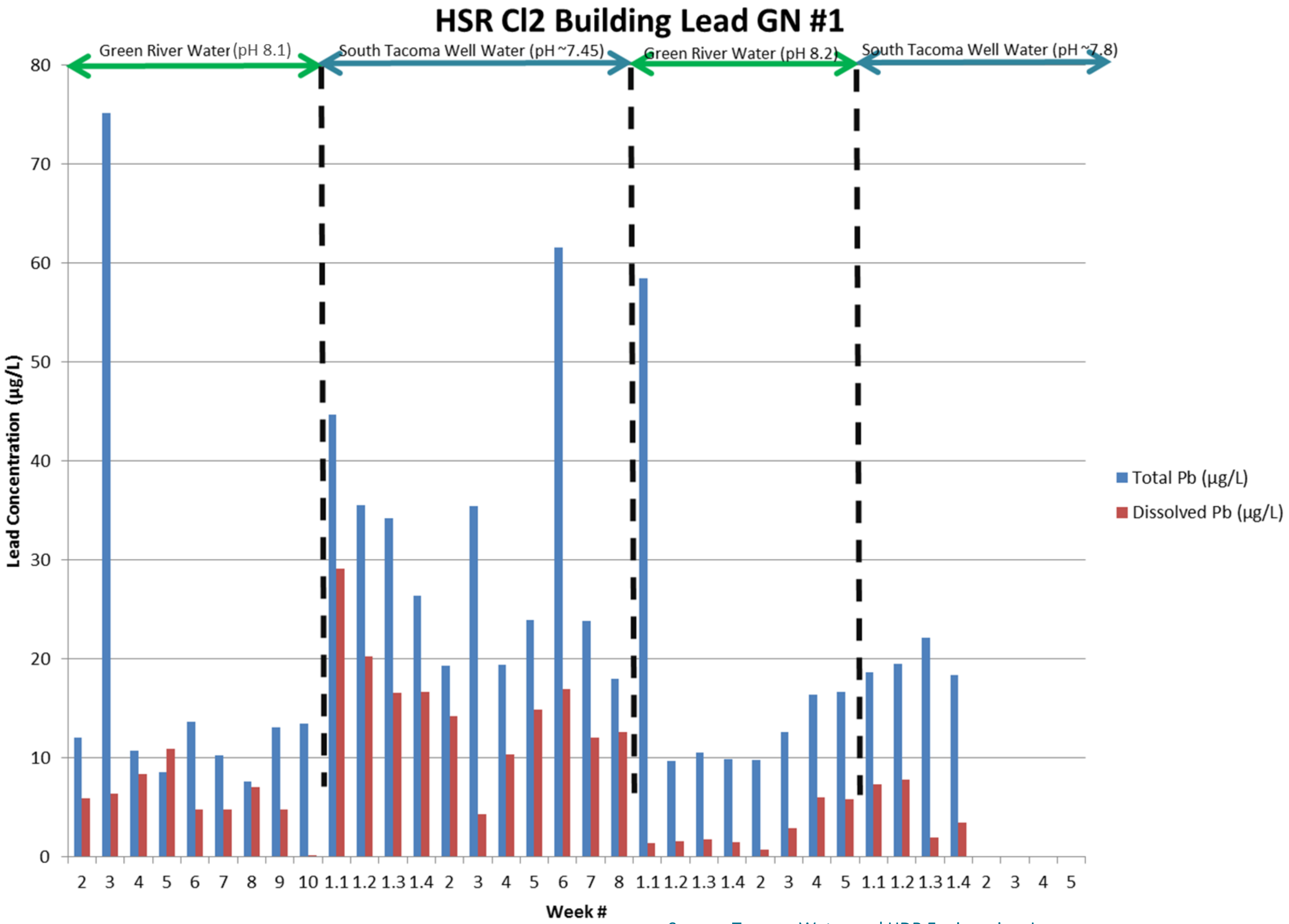
Source: Tacoma Water and HDR Engineering, Inc.

Theoretical Pb Solubility of SW and GW Supplies



- GW less corrosive below pH 8
- SW less corrosive above pH 8
- match solubility
- Because of DIC, actually different dominant lead species
  - GW dominated by cerussite
  - SW dominated by hydrocerussite

Lead from Tacoma Water Pilot Rig Gooseneck 1

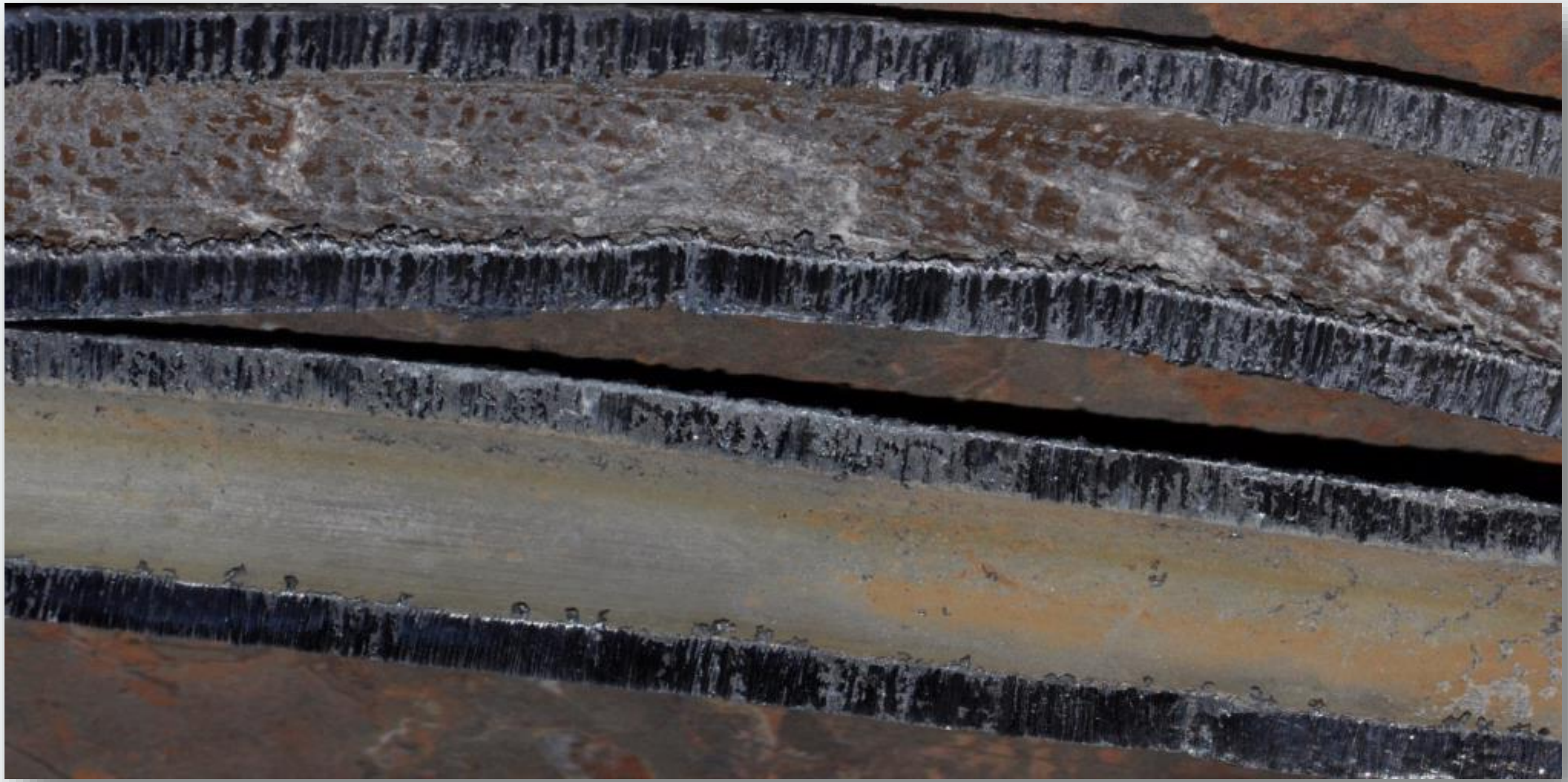


Source: Tacoma Water and HDR Engineering, Inc.

Visual examination of lead gooseneck

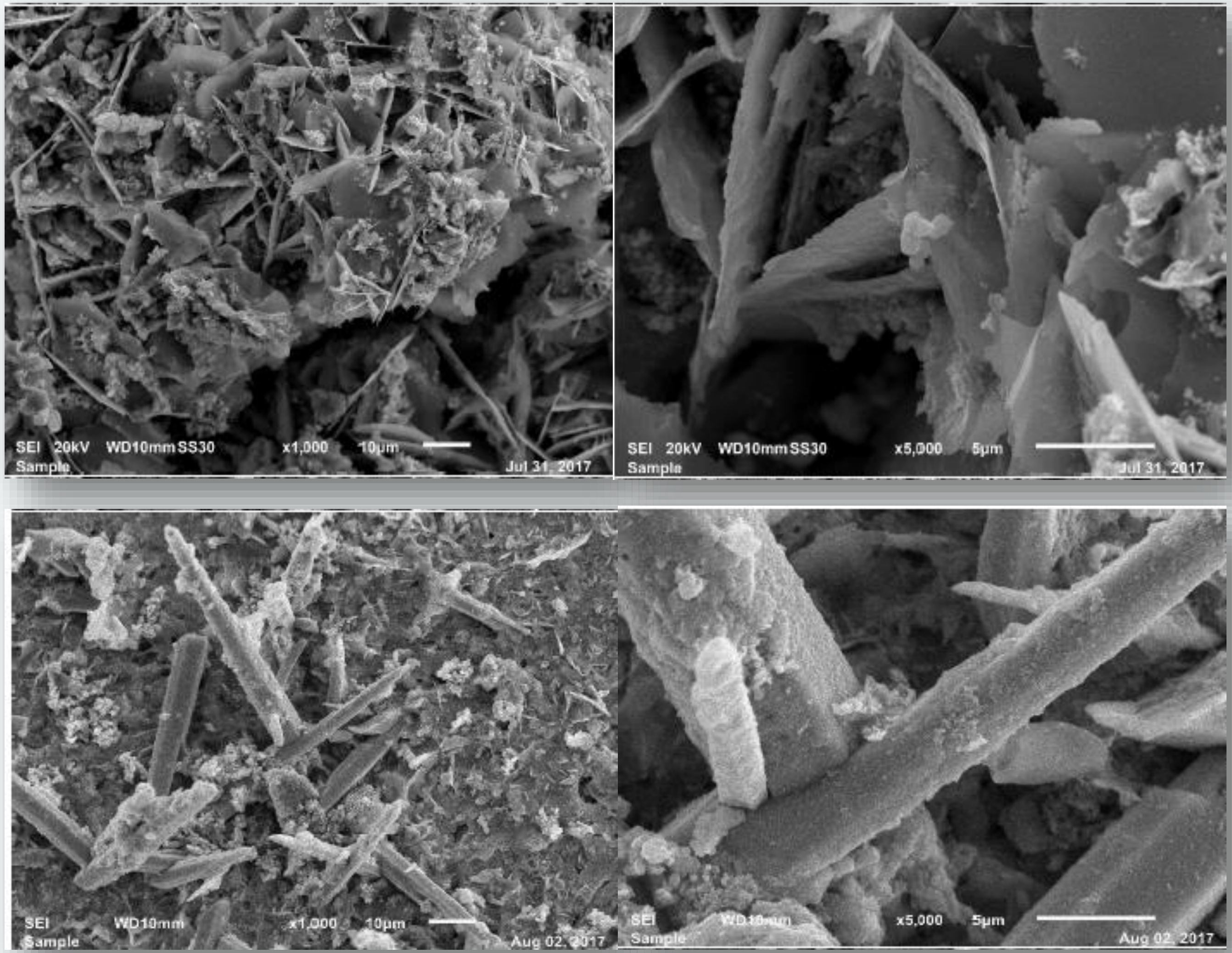
Phase 1 – Surface Water

Phase 2 – Ground Water



Source: G. Korshin, U. Washington

Comparison of Scale Characteristics – SW vs. GW

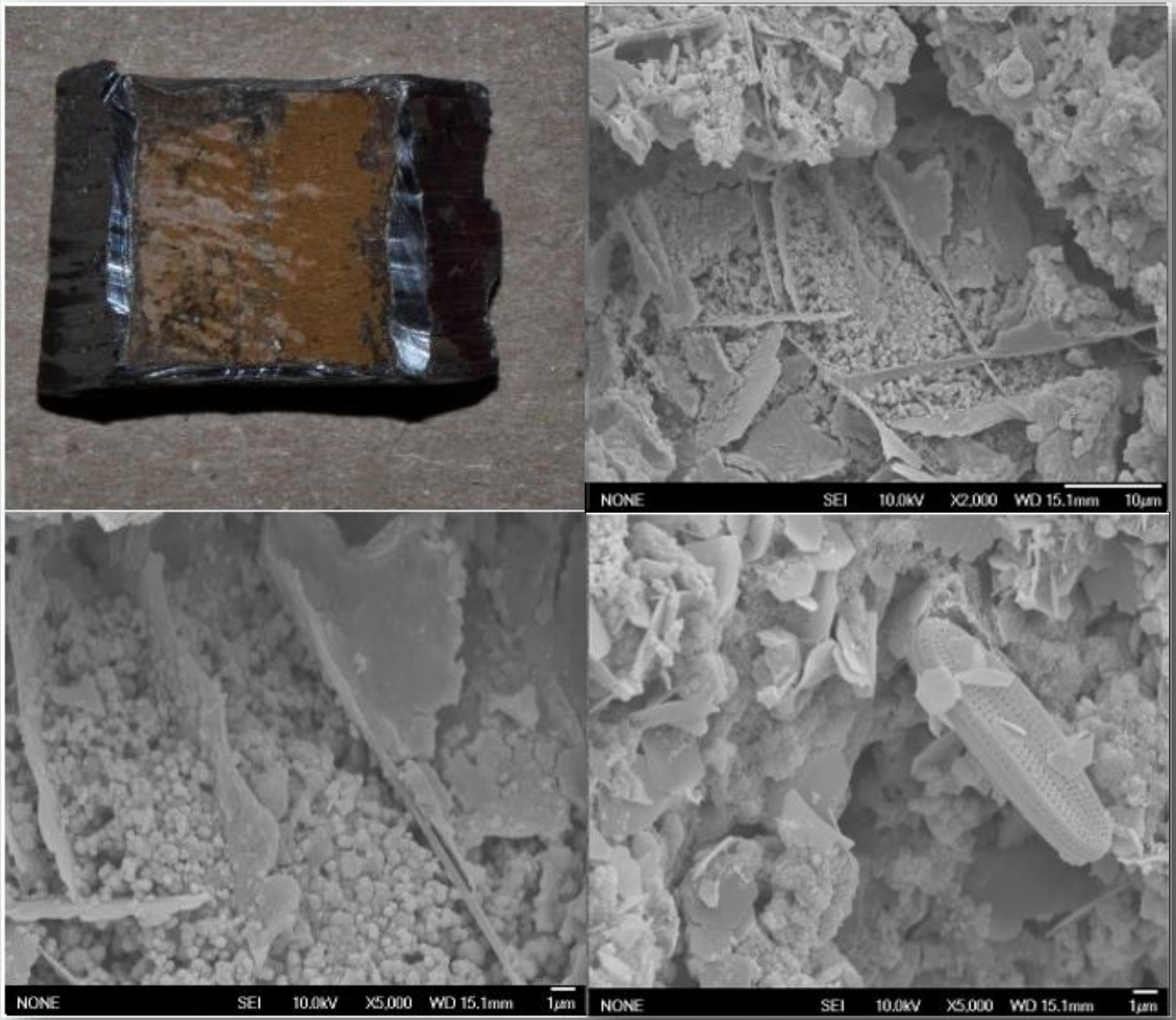


Source: G. Korshin, U. Washington

Lead Gooseneck Phase 1 – Surface Water
Scale dominated by Pb(II) hydrocerussite with some Pb(IV)

Lead Gooseneck Phase 2 - Groundwater
Scale dominated by Pb(II) cerussite with some Pb(IV)

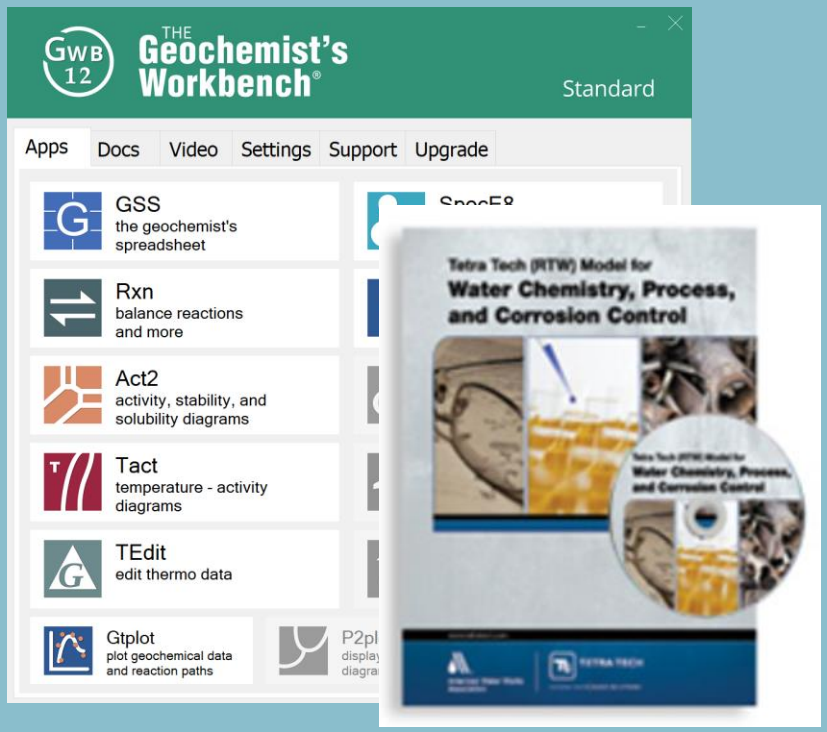
Additional Views of Surface Water Exposed Lead Scale

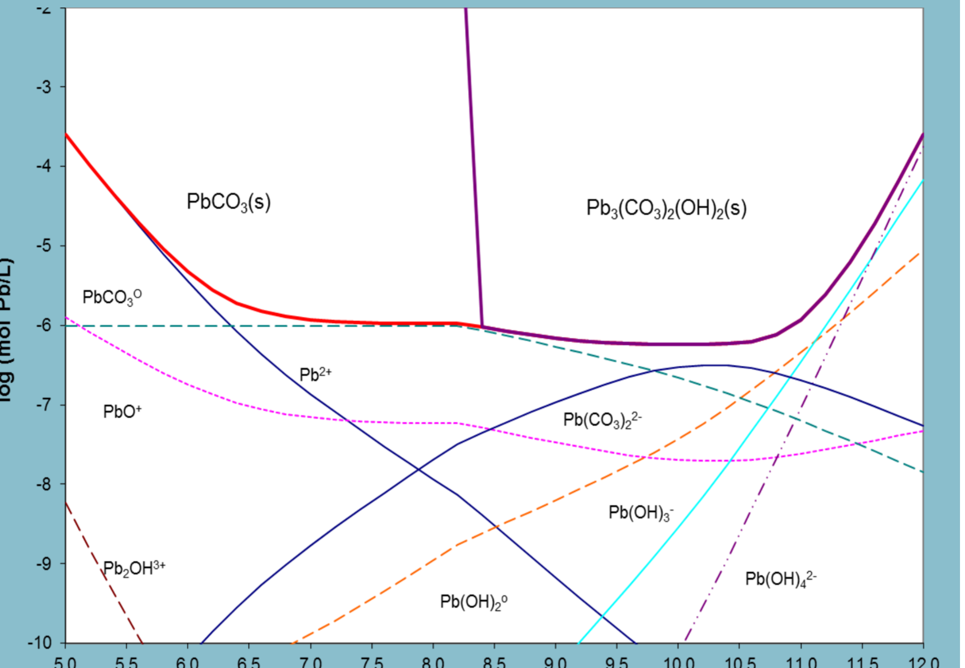


Source: Korshin, U. Washington

Case Study Summary

- Switching between SW and GW can impact lead release
  - Impacts lead speciation
  - Can increase particulate release
  - Very difficult to reach an equilibrium when switching often
- Not enough to just match pH
  - Stable pH still very important for many distribution system reactions
- Alkalinity/DIC play major role
  - Beyond just buffering capacity
- Range of tools used in this study
  - Desk top/Theoretical modeling
  - Pilot rigs to look at lead release
  - Scanning Electron Microscopy (SEM) to look at scale structures
  - Energy Dispersive X-Ray (EDX) also used- results not shown





Conclusions and Recommendations

- Models are great tools, but should never be used on their own to answer CCT or WQ questions
- Models assume conditions at equilibrium
  - The time component to reach equilibrium under varying DSWQ conditions is rarely known.
  - Frequent source water changes likely prevent equilibrium from being reached.
- Models represent specific chemistry conditions
  - Real world distribution system conditions vary considerably seasonally, spatially, etc.
  - Models cannot fully consider impacts of competing ions, other chemical, physical, and microbial conditions that affect scale formation and stability in distribution systems.

But they're still pretty great tools……

THANK YOU

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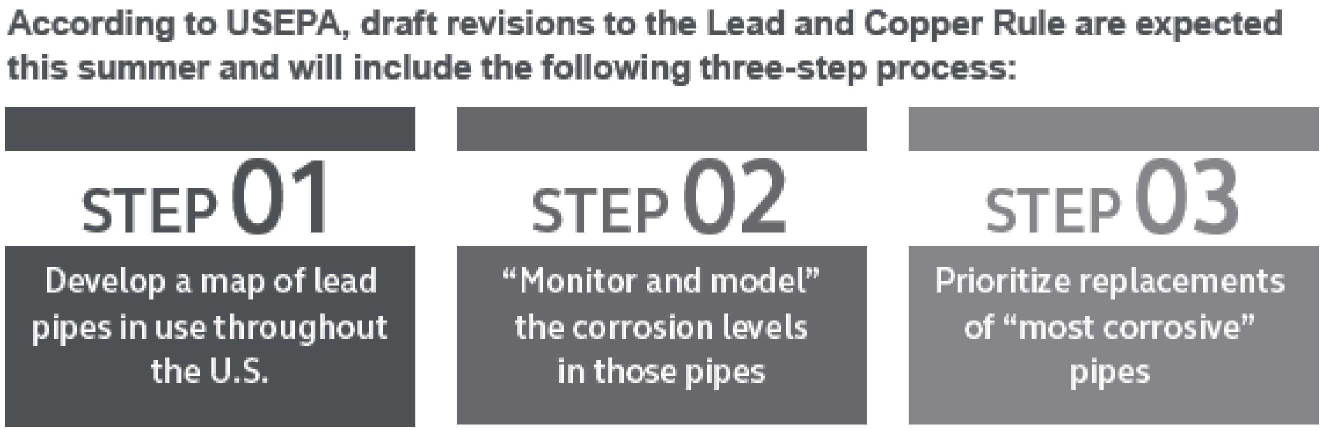
USEPA Long Term Lead and Copper Rule (LT-LCR)

- Options under consideration include:
  - Lead service line replacement,
    - 3-step approach
  - Improving optimal corrosion control treatment requirements,
  - Consideration of a health-based benchmark,
  - The potential role of point-of-use filters,
  - Clarifications or strengthening of tap sampling requirements,
  - Increased transparency, and
  - Public education requirements
- Potential timetable
  - Draft regulation summer 2019?
  - Final rule 2021?
  - 3 years for implementation = 2024?



Source: Arcadis Engineering

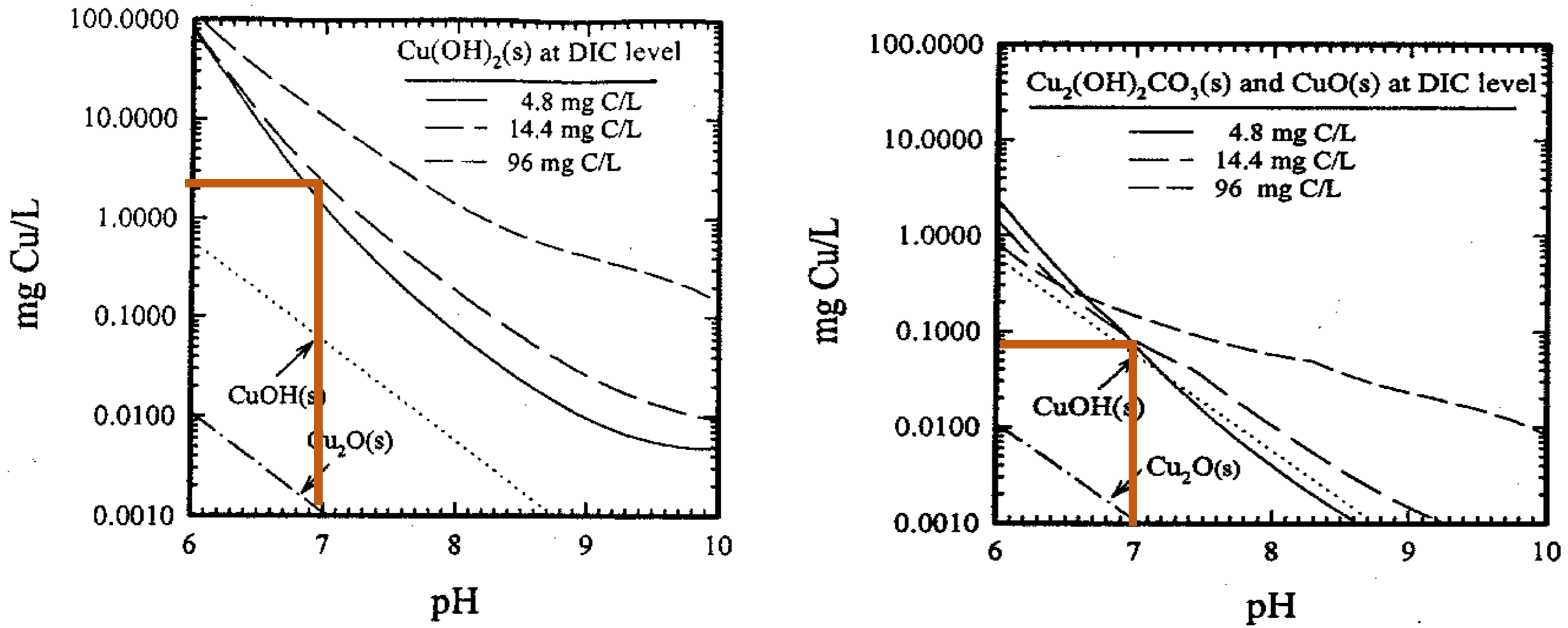
Michigan's New Rule – Finalized in June, 2018 and Effective January 1, 2025

- Reduced lead Action Level to 12 ppb (from 15 ppb)
- Requires CCT study with any new source introduction. Must also maintain OCCT when introducing new source.
- Defined "lead service line (LSL)" as including goosenecks, pigtails, any lead fitting
- DS Materials Inventory
  - Preliminary by January 1, 2020
  - Final, verified by January 1, 2025
  - Update every 5 years afterwards
- Must replace all LSLs at rate of 5% per year, not to exceed 20 years
- Tap Sampling
  - Must come from homes with LSLs if present
  - 1st and 5th liter
  - Cannot reduce to 3-years unless no LSLs or three annual rounds ≤ 5 ppb lead/650ppb copper
- WQPs
  - Only reduced to annual (no more every 3-years)
  - Expanded to include chloride and sulfate

Health Canada

Copper Solubility

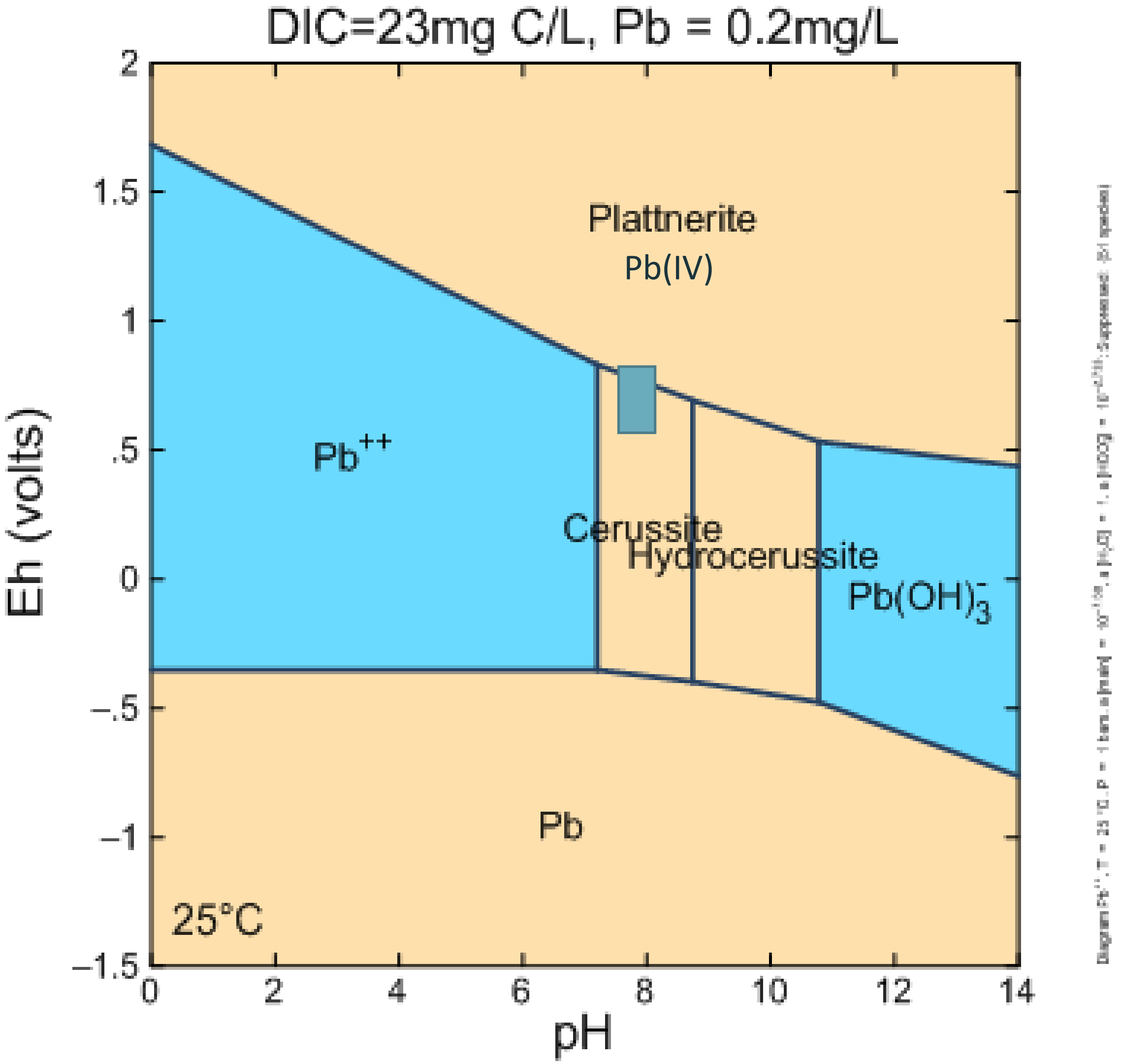
- Water quality & age of scales play key roles – New copper surfaces are most prone for corrosion and higher copper solubility



Copper scales – example at high DIC and Copper(I) and (II) Solubilities at Different DIC Levels (at I = 0.01, 25°C) for: a) New Pipe with $Cu(OH)_2(s)$; b) Aged Pipe. (Schock and Lytle 2011)

Pourbaix Diagram - Lead Speciation as a Function of ORP, DIC, and pH

Groundwater



Surface Water