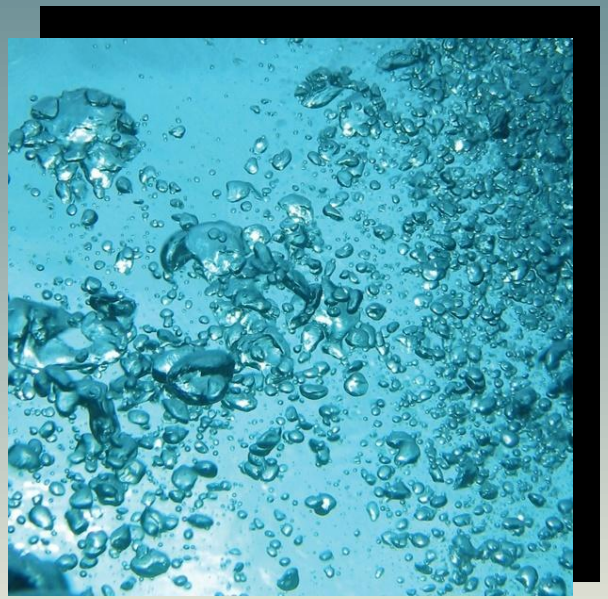
Emerging Concerns of Manganese in Drinking Water

Beyond Aesthetics



AWWA-PNWS Conference
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Confluence Engineering Group

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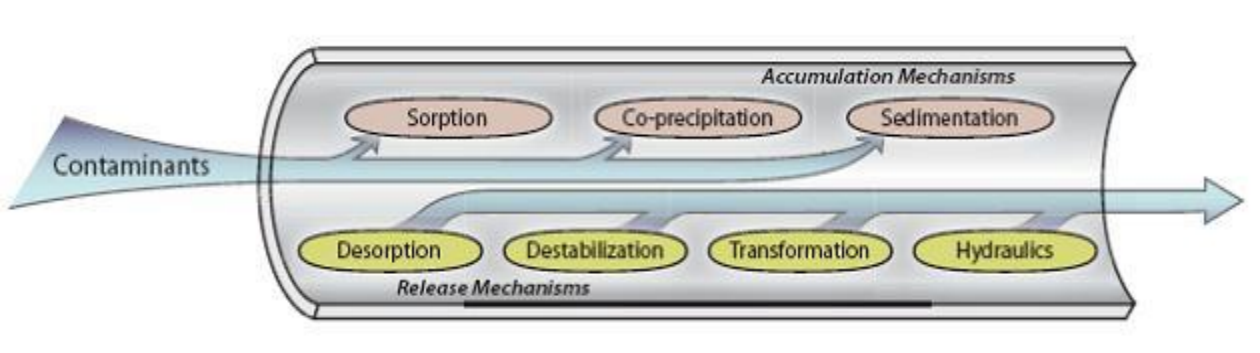
Presentation Overview

- **Background**
  - Traditional View of Mn Issues
- **Emerging Issues**
  - Mn Health Effects
  - Mn-Supported Accumulation of Trace Contaminants
- **Utility Guidance**
  - System Assessment
  - Mitigation and Control

Context of Discussion

- **Behavior within the distribution system**
  - Non-conservative behavior: in ≠ out
  - DS isn't just a conduit – it's a reactor



Numerous mechanisms can affect contaminant fate and transport within distribution systems, resulting in "non-conservative" water quality at-the-tap.

Traditional View of Mn Issues

- **Only an aesthetic problem…**
  - Very low aesthetic threshold (< SMCL)
  - Staining/spotting of laundry, fixtures, etc.
  - Brown/black discoloration, metallic taste

Low-level Mn residuals can cause staining and discoloration, prompting customer complaints.

Thursday, May 20, 2010

Pennichuck blames loosened manganese flecks

By PATRICK MEIGHAN
Staff Writer

Print Share 4 Comments

NASHUA – If you noticed a fine pepper in your drinking water this morning, don't worry, Pennichuck Water Works officials say.

It's a chemical compound called manganese that is brought out by the annual spring flushing of water lines.

A naturally occurring substance, manganese isn't harmful if ingested, said Donald Ware, Pennichuck's president of regulated water utilities.

But it isn't pretty either.

"It's not aesthetically pleasing," Ware added.

Manganese has a dark color, a taste and an odor, he said.

And there's more of it in than in the past because of a change in the chemical processing that is loosening manganese built up in the water lines, he said.

Staff Photo by Grant Morris Manganese, as collected after flushing several fire hydrants, is seen in a bucket at Pennechuck headquarters in Nashua, Wednesday.

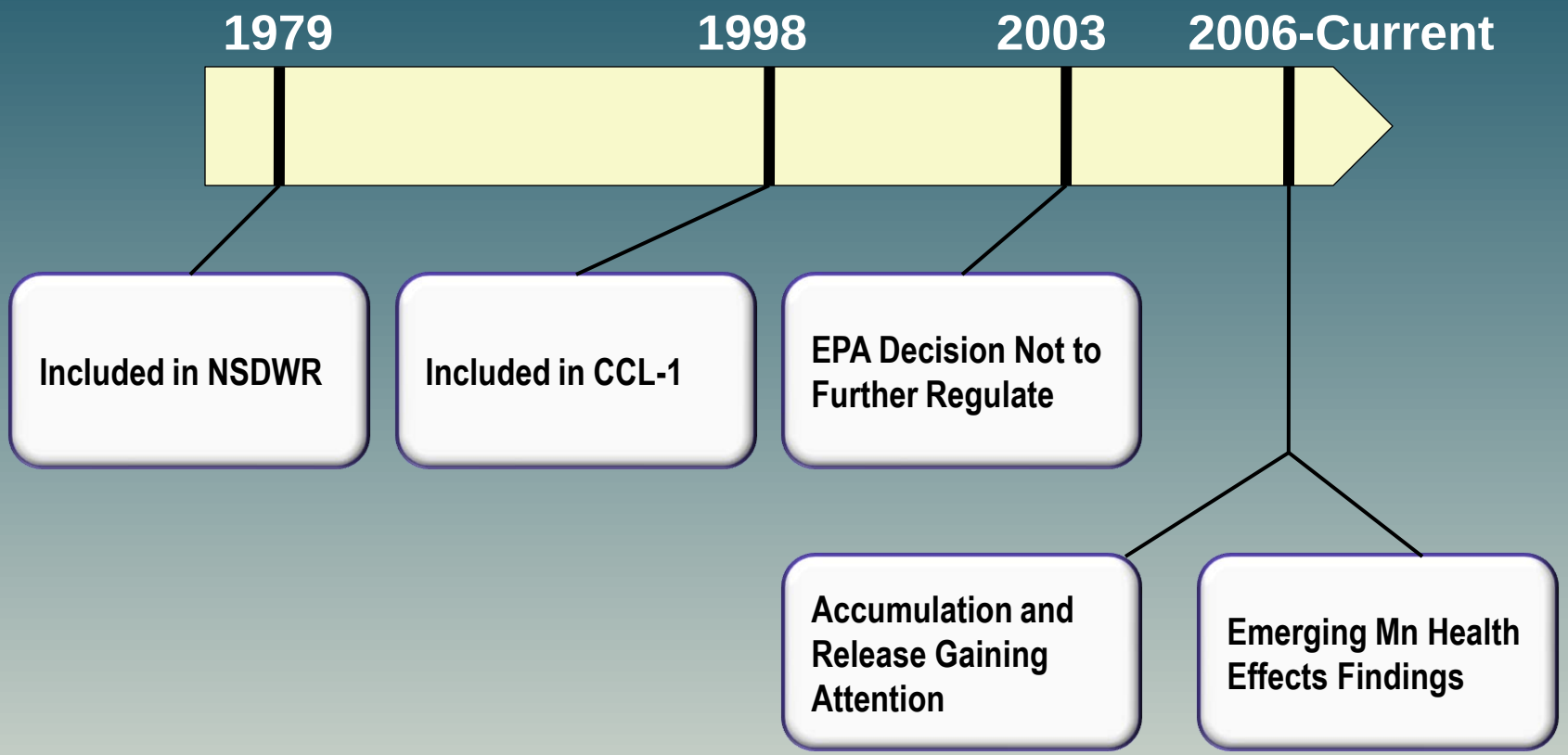
Intermittent but more severe problems include release of Mn coatings and black water events.

Traditional View of Mn Issues (Cont.)

- **Not a health-based or regulatory concern**
  - Unregulated – no federal primary standard
  - SMCL of 0.05 mg/L << levels of health concern
  - Accum/release *perceived* as innocuous events
    - Just unregulated compounds?
    - Obvious discoloration – no one would consume

Mn deposits can be re-suspended by dynamic DS conditions, resulting in discoloration at customer taps.

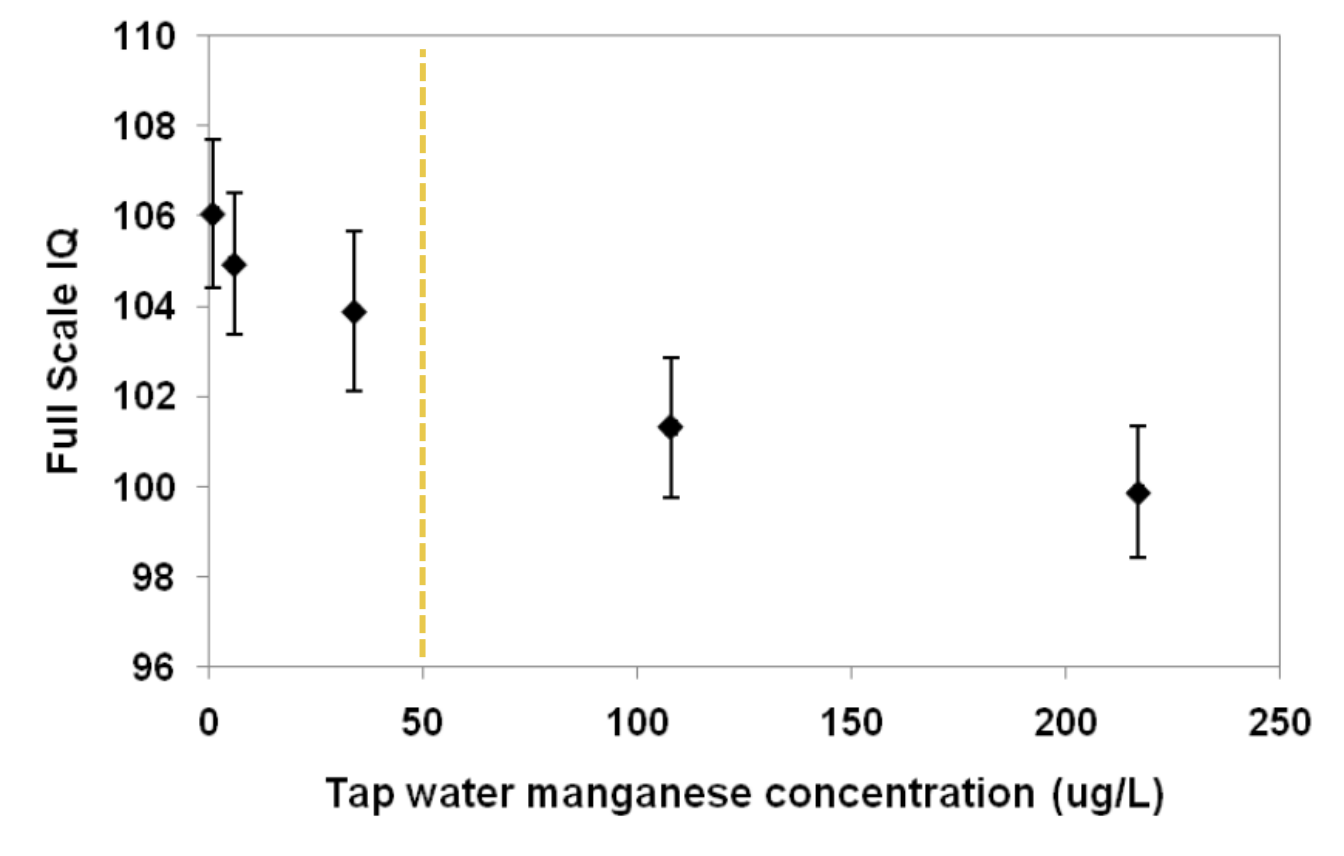
Historical Perspective



Emerging Mn Issue #1: Recent Health Effects Research

- **Concern is with infants and children**
  - Higher absorption and retention rates
  - More susceptible to neurotoxic effects
    - Intellectual performance and memory
- **Multiple research studies published**
  - Different approaches but similar conclusions
    - "Toss out the reference dose model for adults"
    - More research is needed

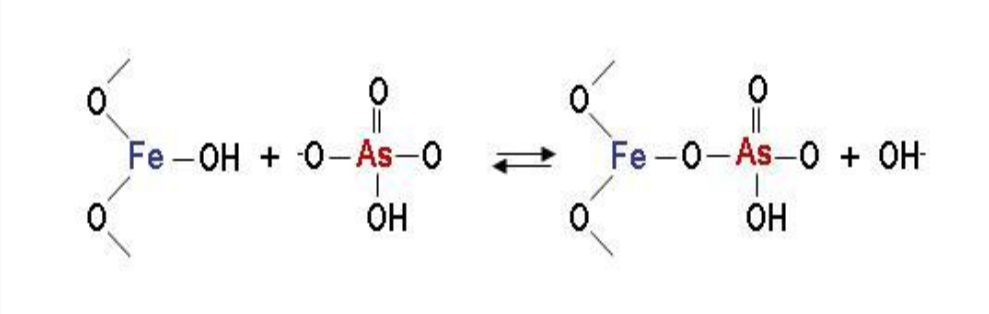
Mn in Drinking Water: Cognitive Effects in Children



Inverse relationship of children's IQ to Mn levels in drinking water (n=362) (Source: Bouchard et al, 2010).

Emerging Mn Issue #2: Accumulation of Regulated Contaminants

- **Trace metal elements and radionuclides**
  - Historical presumption of conservative behavior (in=out)
  - … but now known to accumulate in distribution systems
    - Even when treated water concentrations are very low (or ND)
    - Common un-regulated solids serve as accumulation "sinks"



Adsorption of arsenic onto an Fe oxyhydroxide solid substrate typical of iron corrosion scale.

Emerging Mn Issue #2: Accumulation of Regulated Contaminants (Cont.)

- **Once accumulated, trace contaminants can be released due to dynamic DS conditions**
  - Release not easy to control (or always identify)
  - Can result in elevated concentrations at the tap
    - Excursions >> MCLs have been documented
  - Potential public health implications if consumed
    - Regulatory/monitoring framework misses this

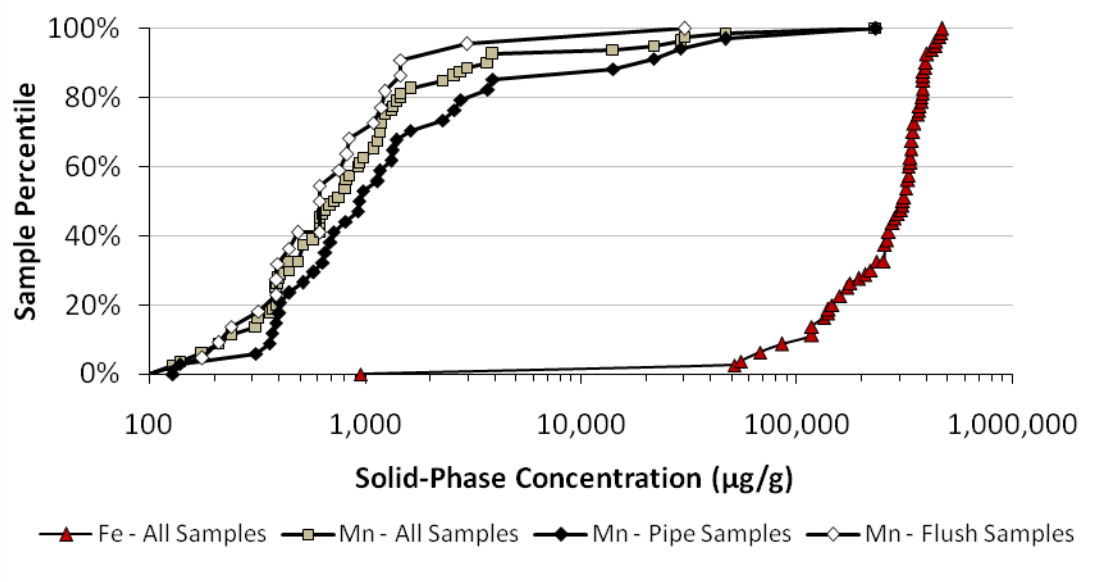
Accumulation Sinks: Fe-Oxide Solids Typically Emphasized

1. **Common component of DS deposits**
   - Highest occurrence in DS deposits (10-40 wt%)
2. **Corrosion scales increase surface area**
3. **Well-known adsorptive properties**
   - Fe coagulant/GFO media used for DW treatment
   - Most effective for trace metal anions (As, U, Cr)

Thick Fe-oxide corrosion scale magnifies the area available for contaminant adsorption.

Accumulation Sinks: Mn-Oxide Solids Gaining Attention

1. **Ubiquitous in DS deposits**
   - Fraction of Fe levels
   - High variability, affected by site-specific conditions
     - POE Mn levels, water chemistry, hydraulic conditions, pipe type, utility maintenance practices, etc.



Fe and Mn occurrence levels in 72 solid samples obtained from 20 utility systems for WRF #3118. Finished water Mn levels were 0.3–55 µg/L.

Accumulation Sinks: Mn-Oxide Solids Gaining Attention (Cont.)

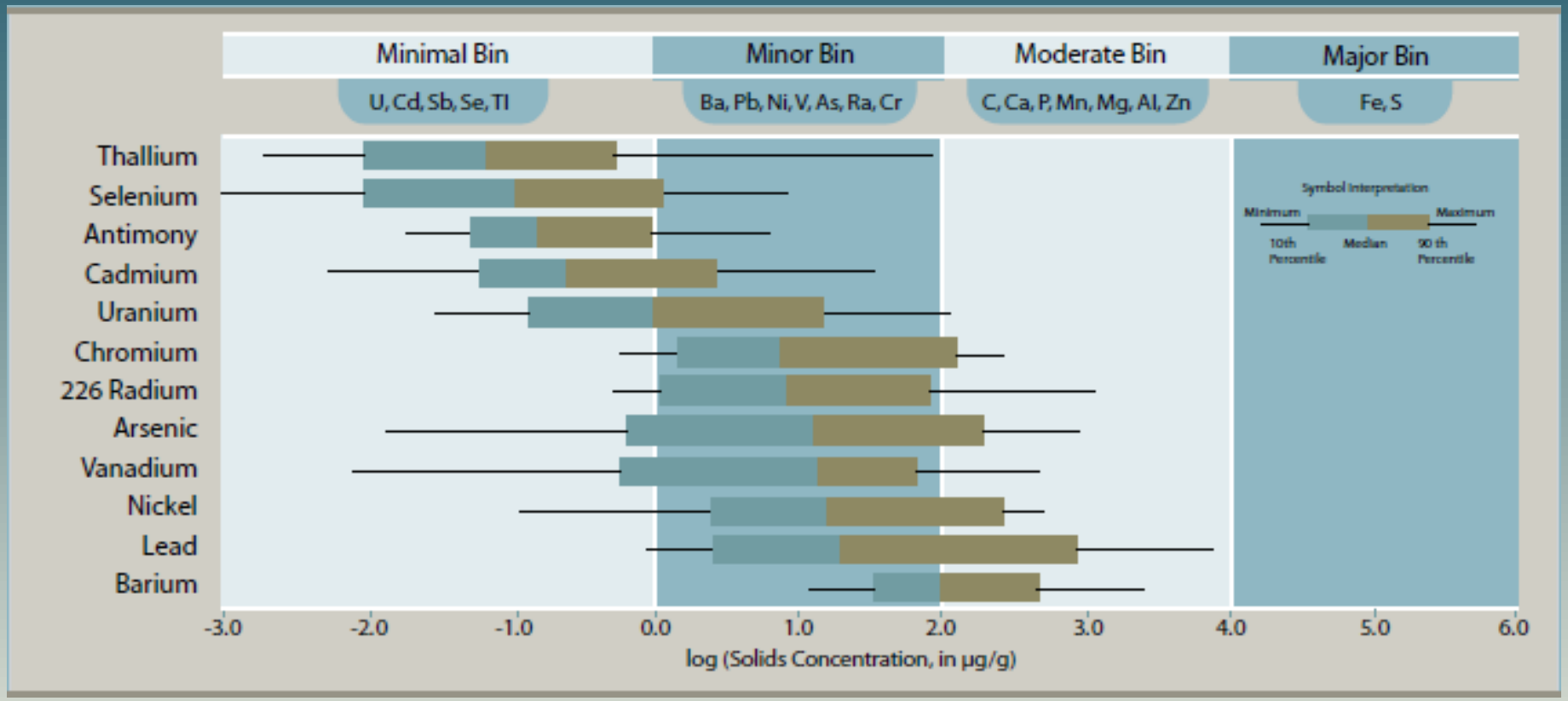
1. **Ubiquitous in DS deposits**
2. **Substantial surface area**
   - Forms thin coatings at water-solid interface (high A:V)
   - Specific area of 350-450 m^2/g (vs. 100-200 m^2/g for Fe)

Mn-oxide deposition is typically as a thin film or coating on pipe surfaces and corrosion scales.

Accumulation Sinks: Mn-Oxide Solids Gaining Attention (Cont.)

1. **Ubiquitous in DS deposits**
2. **Substantial surface area**
3. **Highly-reactive surface chemistry**
   - Applications in DW treatment
     - MnO_2 media used for Mn^{2+}
     - HMO solids for Ra^{2+}
   - Natural analogs: scavenging of Pb, Cd, Cu, etc.
     - Trace metal cations

WaterRF 3118 – Occurrence Profiles



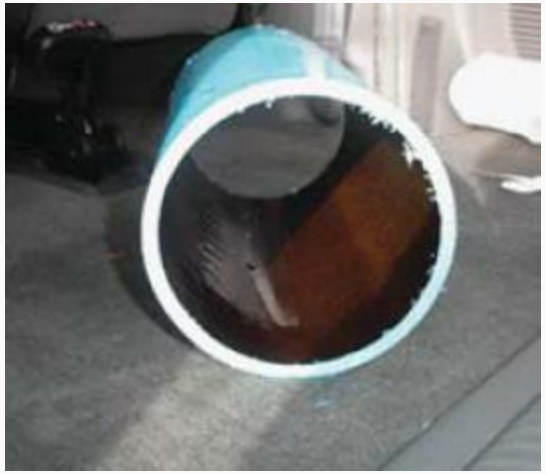
Influence of Mn in Real-World Deposits

- **Apply linear adsorption model to occurrence data from WRF 3118**
  - Real-world, heterogeneous DS deposits
  - Determine relative impact of Mn vs. Fe
  - Focus on highly-occurring trace metals

Trace Element	$K_{d,Mn} / K_{d,Fe}$	Regression R^2
Barium	~150:1	0.60
Lead	~50:1	0.60
Nickel	~100:1	0.90
Radium	~200:1	0.95

Influence of Mn in Real-World Deposits

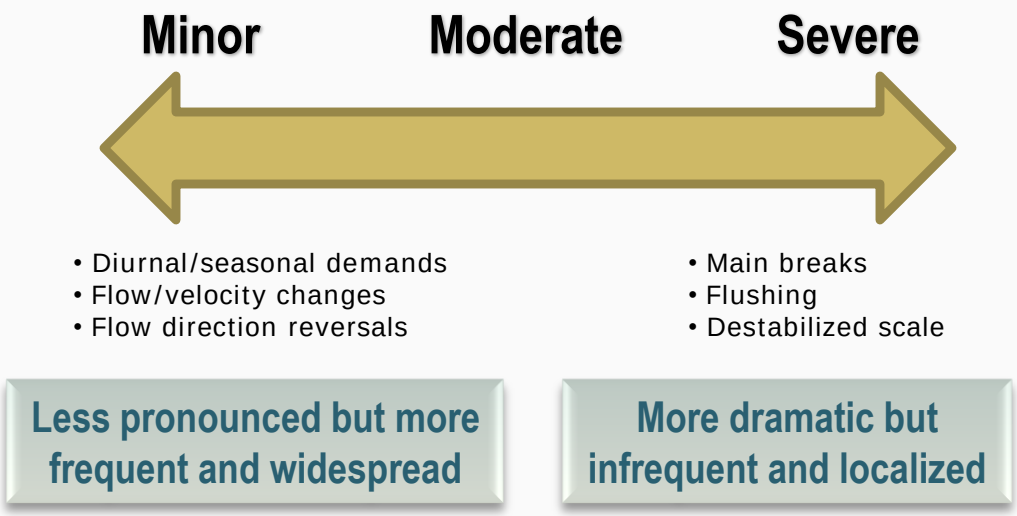
- **Mn exerts an influence far out of proportion to its concentration**
  - Significant contribution to accumulation of several trace inorganics despite being present at a fraction of Fe level
  - Outright "control" for high residual Mn conditions and in non-corrosive pipes



- **Implications**
  - Contaminant release potential
  - Control of contaminant levels

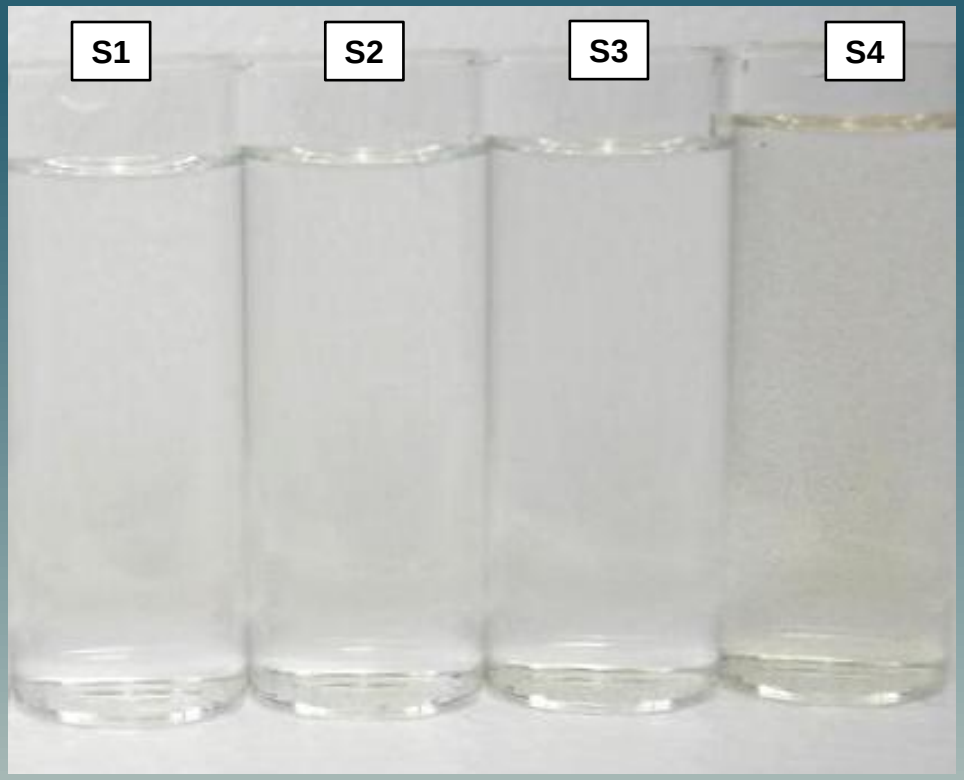
Hydraulic Release

- **Re-suspension of solids-associated contaminants**
- **Possible discoloration and turbidity**
  - Depends on amount and type of solids released



Simulated Mn-Associated Lead Release

- [Pb] of 0.5 µg/L
- Pb:Mn 50 mg/g



Parameter		S1	S2	S3	S4
Particulate Mn	mg/L	0.003	0.05 (SMCL)	0.30 (HAV)	1.00
Total Lead	ug/L	0.65	3.0	15.5	50.5
Turbidity	ntu	0.01	0.2	0.4	1.1

Guidance to Utilities

- **System Assessment**
  - Mn and trace inorganic occurrence
  - Hydraulic and chemical releases
- **Mitigation and Control**
  - Remove legacy Mn solids
  - Reduce on-going loading

Conclusions

- **Mn in DW presents previously unrecognized risks**
  - Possible health impacts in children at levels comparable to SMCL
  - Plays a key role in the accumulation/release of toxic trace metals
- **Mn deposition in DS magnifies the accumulation of trace contaminants**
  - Non-trace amounts even when low-to-ND in treated water
  - Mn is the controlling substrate in some instances
  - Surficial nature increases hydraulic mobilization risk
- **Multi-faceted approach needed to control**
  - Monitoring
  - System O&M
  - Treatment

Questions?

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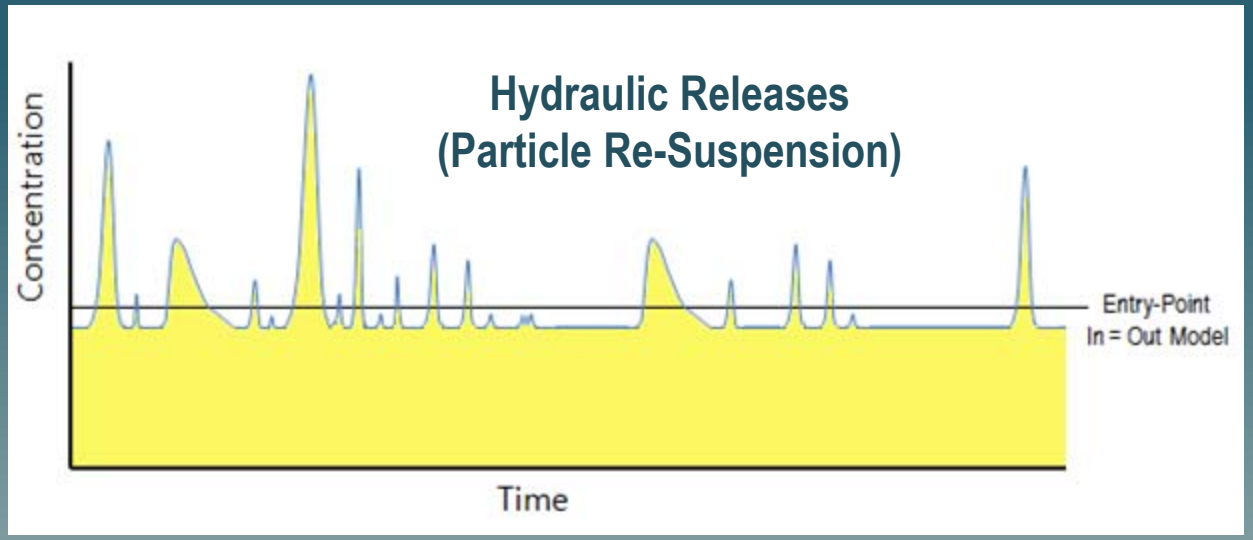
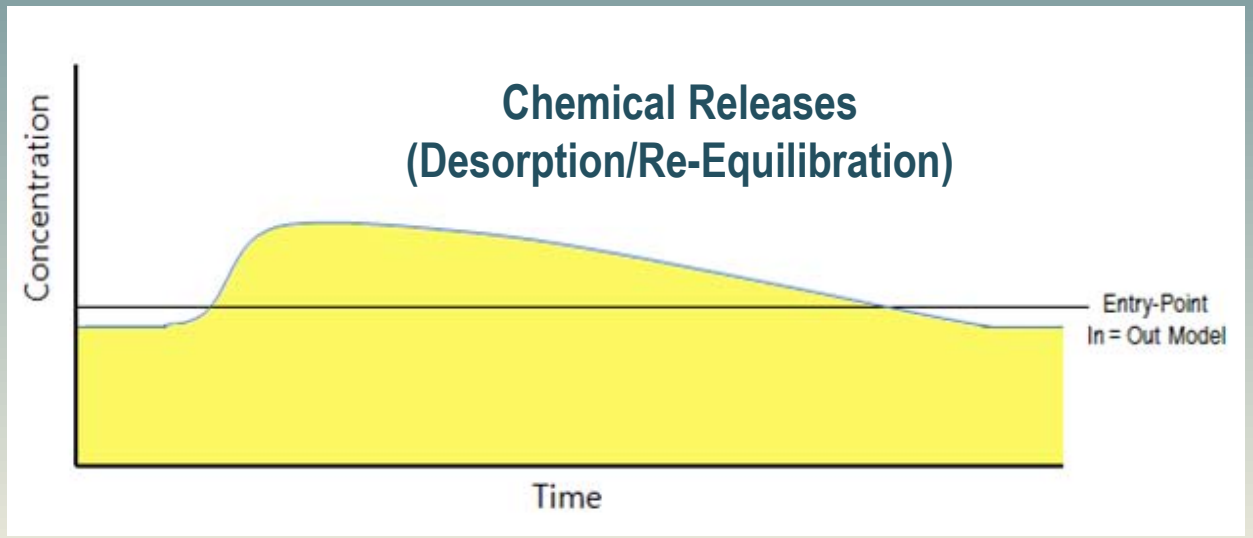
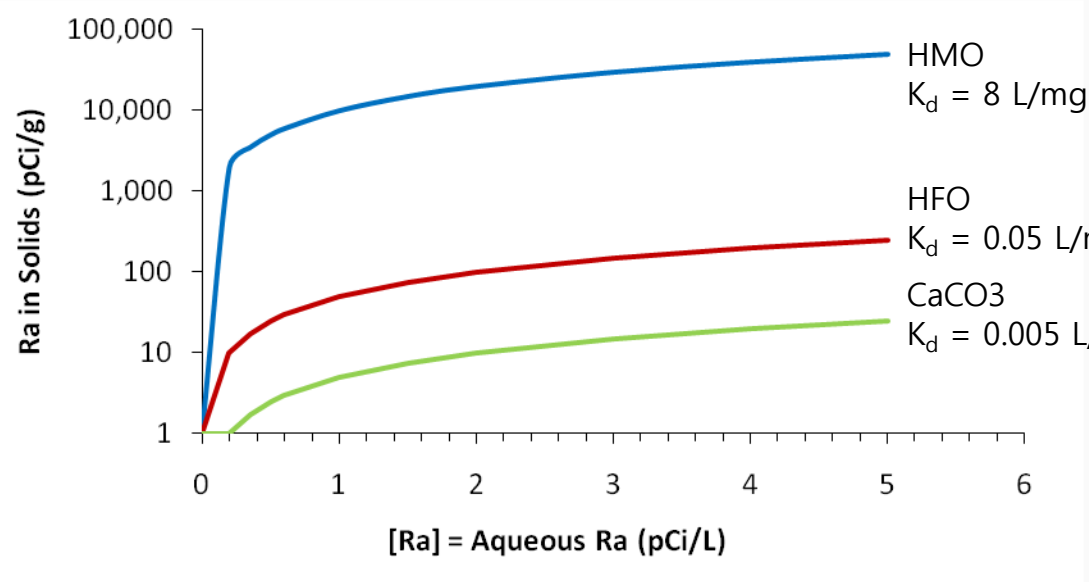
Conceptual Contaminant Profiles





Comparison of Adsorption Capacities

- **Linear isotherm model for adsorption**
  - $q_A = K_d [A]$
  - K_d indicates relative sorption capacities of different solids for a given contaminant "A"



Equilibrium isotherms for radium adsorption onto synthesized solids typical of DS deposits, at pH 7.5. (source: Valentine, 1990).

System Assessment

- **Evaluate at the individual utility level**
  - Capture system- and site-specific factors
- **Prioritize portions of the system**
  - Use established risk factors as guidance
- **Plan and perform monitoring within DS**
  - Collection/analysis of pipe specimens and flush solids
  - Bulk water sampling to gauge release potential
  - Monitoring protocol for flushing and response
    - Reliable methods for Mn, color
    - System-specific correlation to IOCs

Flushing to Capture Deposits

Special socks can be used to capture solids from hydrant flushing events.

Mitigation and Control

- **Address legacy deposits and contaminants**
  - Be proactive and "preventative" in getting the stuff out
    - Focus on prioritized and at-risk areas
  - Remove "loose" deposits – Physical Release Control
    - High-velocity unidirectional flushing
    - Avoid conventional flushing
  - Stabilize adherent deposits – Chemical Release Control
    - Pigging or cubing
    - Pipe rehab/replacement
    - Stabilize water chemistry

Cubing – Compressible Pigs

Mitigation and Control (Cont.)

- **Reduce on-going loading**
  - Mn ≤ 0.01 mg/L
  - Trace inorganic contaminants
    - Lowest practicable levels
    - Avoid side-stream or blending
- **Install or optimize treatment**
  - Oxidation – filtration → Co-removal
    - Benefit of Fe/Mn in source water
    - Purposeful addition to optimize IOC removal