The Occurrence of Contaminant Accumulation in Lead Pipe Scales from Domestic Drinking Water Distribution Systems

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Scope of Study

Overall Scope and Objectives

- **Over 191 Lead and lead-lined pipe samples from municipal water systems have been received and analyzed since 1989**

- **91 samples had sufficient scale for reasonably-complete elemental analysis**

- **This subset encompassed**

  - **26 municipal water systems**
    - **15 treated surface waters**
    - **9 treated ground waters**
    - **2 systems with pipe exposed to a mix of GW and SW**
  - **8 states**
  - **Span of 16 years**

- **No MCL violations for inorganics (other than Pb or Cu) in period studied**

Geographical Distribution of Pipe Specimens
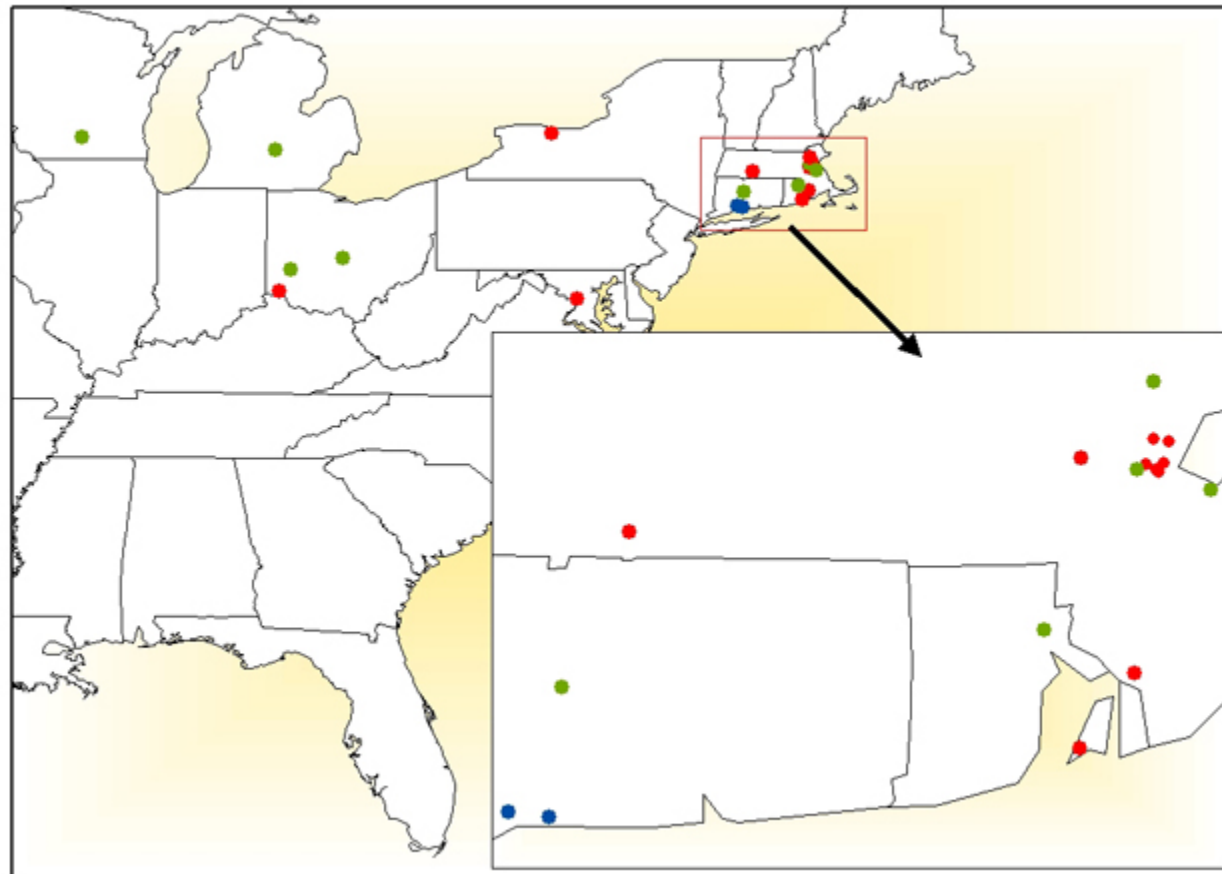
Red dot = Surface water

Green dot = Ground water

Blue dot = Mixed sources

Objectives

- **To take advantage of "samples of opportunity" from ongoing studies relating to corrosion control modeling for lead plumbing materials**

- **Test hypotheses about the likelihood of accumulation of non-Pb elements and compounds in diverse water chemistries**

- **If confirmed, use as a starting point for future studies**
  - **Determine speciation of contaminants of interest**
  - **Investigate vulnerability to destabilization or release by water quality changes or hydraulic disturbances (theory and experimental)**
  - **Investigate potential differences in capacity and potential for accumulating particular contaminants with different types of pipe surfaces**
    - **Corrosion products**
    - **Post-precipitation**

- **Develop guidance for improved monitoring strategies to protect consumers**

Analytical Methodology

Initial Pipe Sample Processing

- **Upon receipt**
  - **End coverings checked for openings**
  - **If not covered, ends are capped**
  - **External material scrubbed off to the extent practical**
- **End coverings removed, loose material (if any) collected for later comparison and possible analysis**
- **Pipe scale is allowed to air dry at room temperature**
- **Pipes are labeled and cut longitudinally with bandsaw (fine-toothed carbon steel blade)**
- **For Pb pipes, number of pipes per blade limited by clogging of teeth**

Pipe Examination (1)

- **After cutting, Pb debris removed with air and/or variety of tools**
  - **Dental picks**
  - **Soft brushes**
  - **Forceps**
- **"Macro" photographs taken, and physical properties of scale noted**

Pipe Examination (2)

- **Scale "harvesting" begins**
  - **Assortment of fine tools used**
    - **Brushes**
    - **Spatulas**
    - **Dental picks**
    - **Miscellaneous other tools**
  - **Operationally-defined, based on:**
    - **Texture**
    - **Color**
    - **Position (on surface and relative to other apparent layers)**
- **Sequentially numbered layers from outer (L1) to innermost (usually 3, range 2-4)**
- **Mineralogical & textural descriptions using stereomicroscopy**
- **Microphotography**

Solids Preparation

- **Each layer collected:**
  - **Grinding**
    - Mortar & pestle, agate (usual), synthetic ruby
    - Ball mill (agate, tungsten carbide)
  - **Sieving (stainless steel)**
    - To pass 200 mesh (≤75μm)
    - Compromise between ideal for XRD/microbeam methods and reducing differential hardness effects
  - **Split for different analyses**

Example of Layer Differentiation

Analytical Prioritization

- **Pipe lengths and scale characteristics were very variable**

- **Mass of scale harvested varied widely**
  - **10-20 mg minimum**
  - **Rare cases up to 2 or more grams**
  - **"Typical" amount around 200 mg**

- **All samples subjected to XRD analysis**

- **Given sufficient sample, elemental analyses followed a priority scheme**

Elemental Analysis Priority

- **Prioritized until scale aliquot was consumed**
    1. **ICP-AES, 40 elements**
    2. **ICP-MS for Si, REE's**
    3. **Total C + Total S**
    4. **Mercury**
    5. **Total Inorganic C**

ICP-AES

- **USGS** *"Analytical Methods for Chemical Analysis of Geological and Other Materials"*

- **Sequential digestion at low temperature**
  - **Hydrochloric acid**
  - **Nitric acid**
  - **Perchloric acid**
  - **Hydrofluoric acid**

- **Perkin-Elmer Optima 3000 simultaneous spectrometer**

ICP-OES

- **USGS *"Analytical Methods for Chemical Analysis of Geological and Other Materials"* tweaked to improve Si recovery**

- **Sintering procedure**
  - **Sintering with sodium peroxide**
  - **Leaching with water**
  - **Acidifying with nitric acid**

- **Perkin-Elmer Elan 6000**

Other Analyses

- **Total C and Total S**
  - **Combustion**
  - **LECO 230CS**

- **Mercury**
  - **USGS standard method**
  - **Nitric acid/sodium dichromate digestion**
  - **CV-AAS**
  - **P-E 3030B spectrophotometer**

- **TIC**
  - **2 M perchloric acid evolution of CO_2**
  - **Coulometric titration**
  - **UIC, Inc. Carbonate Coulometer 5012**

A Visual Tour of Lead Pipe Scales

High Fe, Mn & Al Scales

$Pb_9(PO_4)_6$ + residual $PbCO_3$
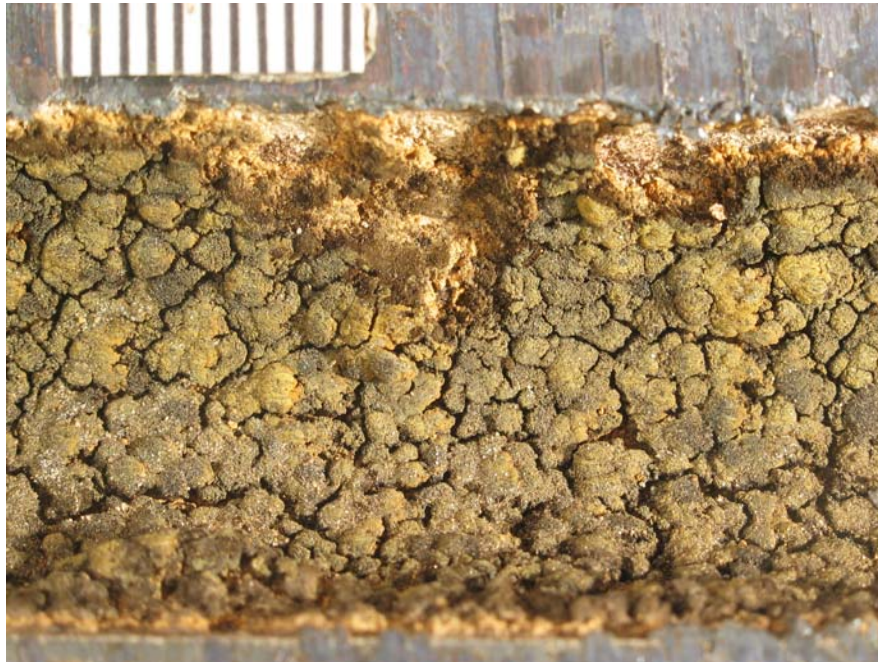
$PbCO_3$ + $Pb_3(CO_3)_2(OH)_2$
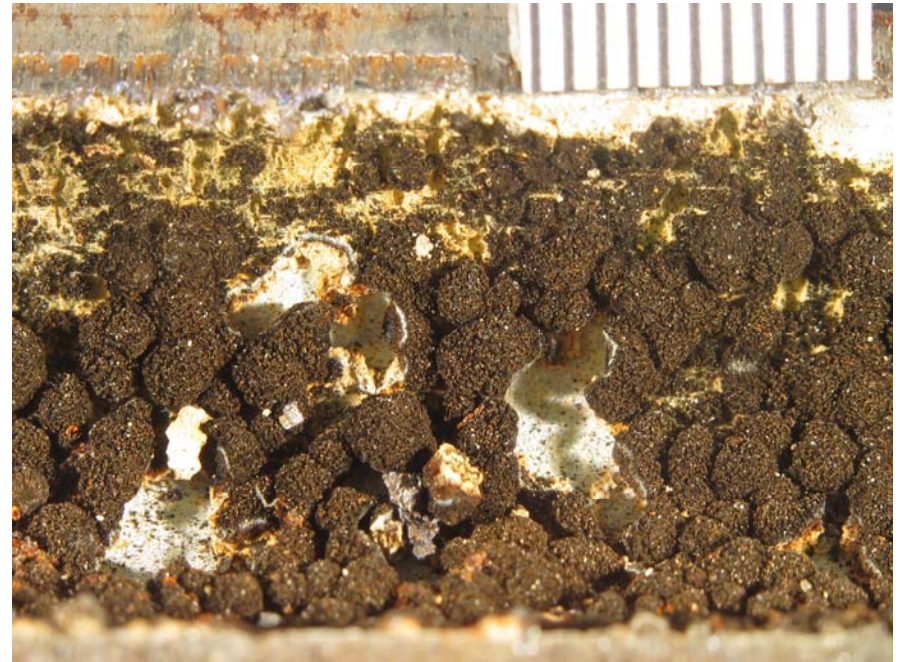
Mostly Amorphous Mn-OH over PbCO$_3$
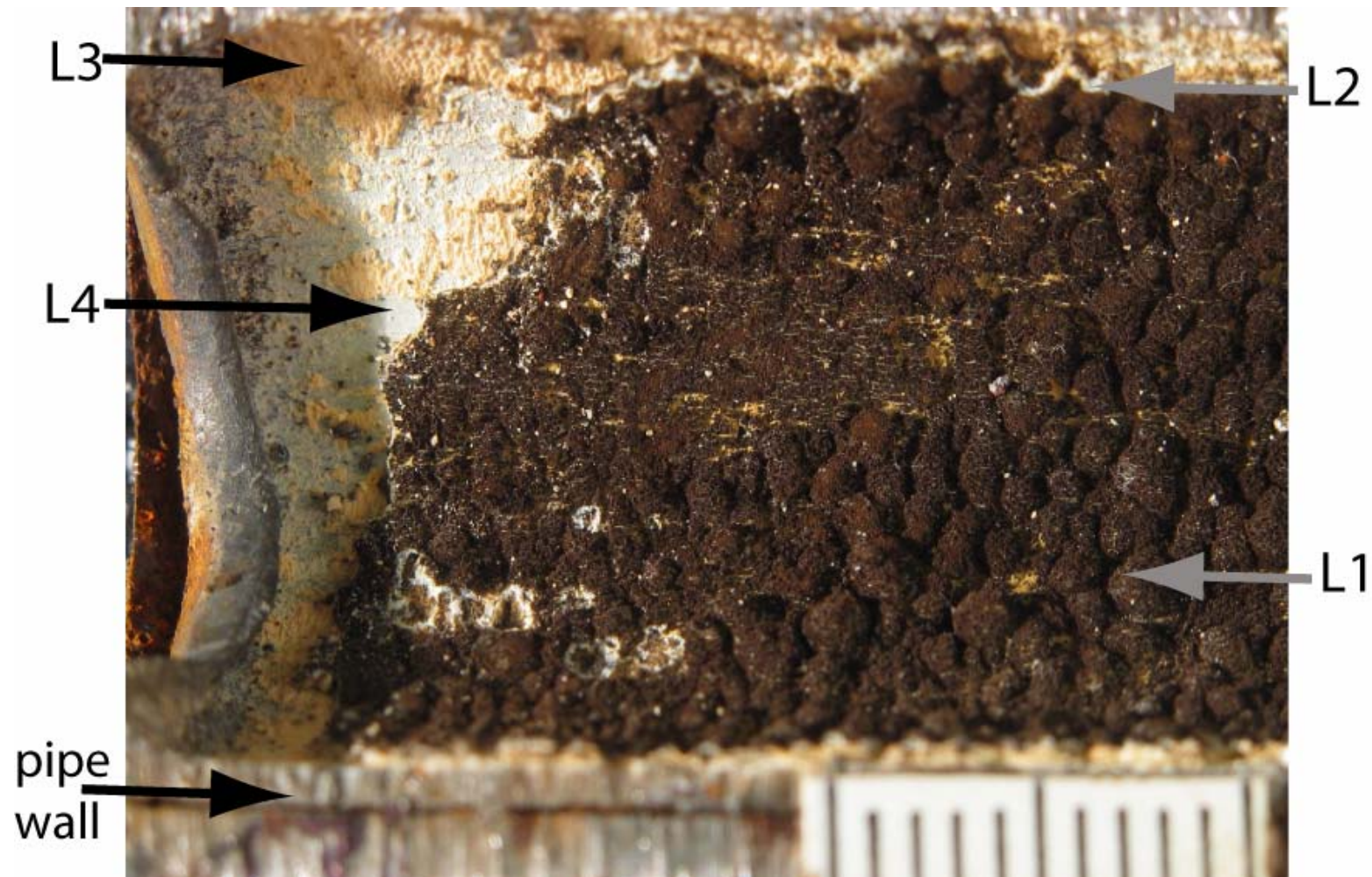
Pb(II) [Hydroxy]Carbonates

Pb Hydroxycarbonates + "Stain"

Primarily PbO₂ Scale

$PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$

Substantial Fe and Al

Data Evaluation

Data Selection

- **Positively *reams* of data were generated**

- **Because of various sample and analytical factors, consistent detection and practical quantitation limits could not be achieved for a given element across all samples and all runs**

- **"Reporting limits" used: reliable results**

- **The usual problem of concentration ranges including non-detects**

- **Sufficient material was not available for all layers of all samples to be analyzed**

Elements Discussed Here
(more analysis to come)

Al	S	V	Mn	Fe
Ni	Cu	Zn	As	Cd
Sn	Ba	Hg	Pb	Bi

Note: Reporting limit for U varied widely across runs

Groupings

- Approximately representing "order of magnitude" occurrence
- Based on averages of data over reporting limit
- <u>Major</u>: > 10,000 mg/kg (>1%)
- <u>Moderate</u>: from 1000 – 9999 mg/kg
- <u>Minor</u>: from100 - 999 mg/kg
- <u>Minimal</u>: 99 mg/kg or below
- Pb largest component in 88 of 91 samples
  - Not extremely reliable because of cutting contamination
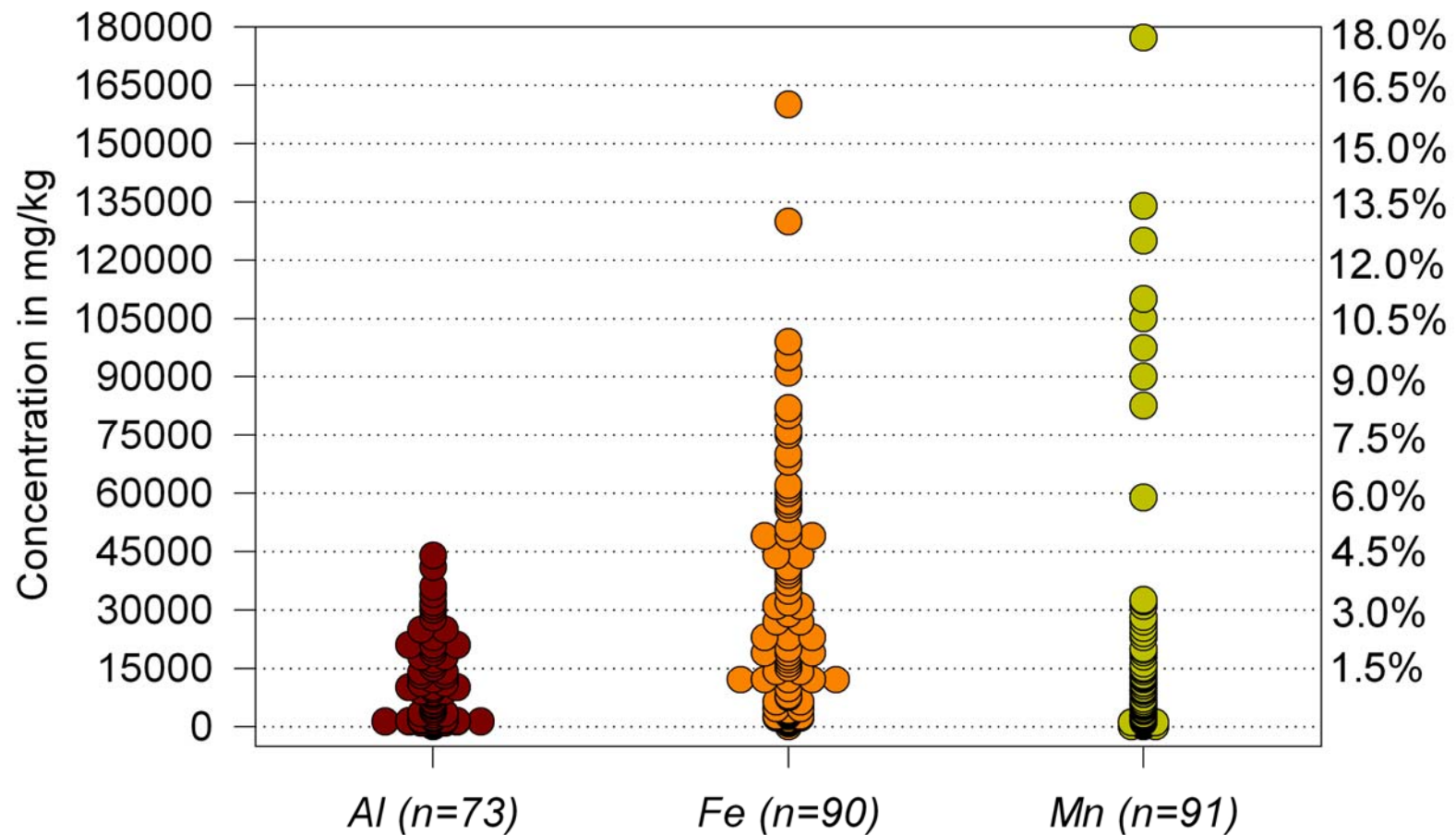
Focus Elements

Major Constituents

Moderate Constituents
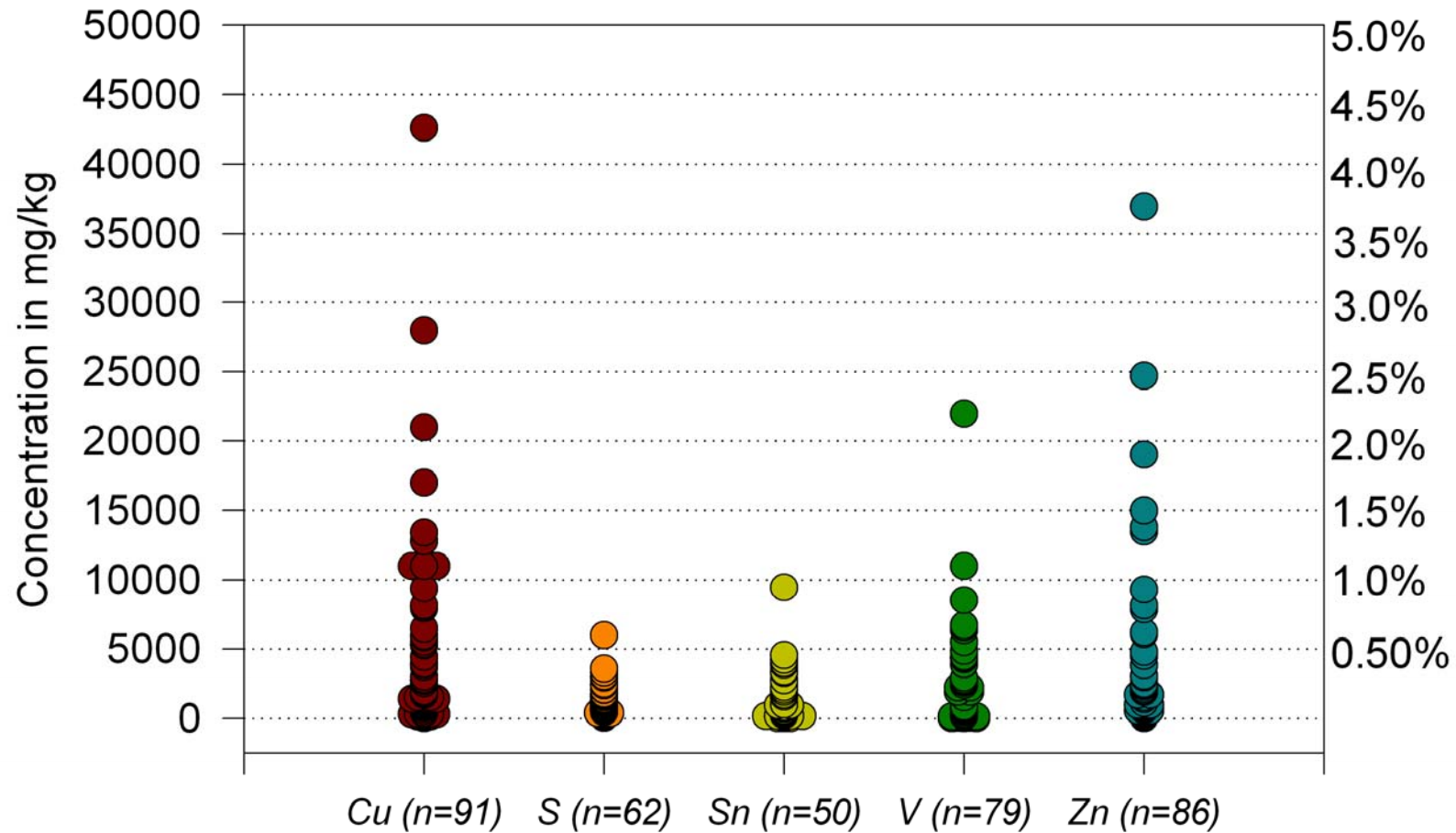
Minimal and Minor Constituents
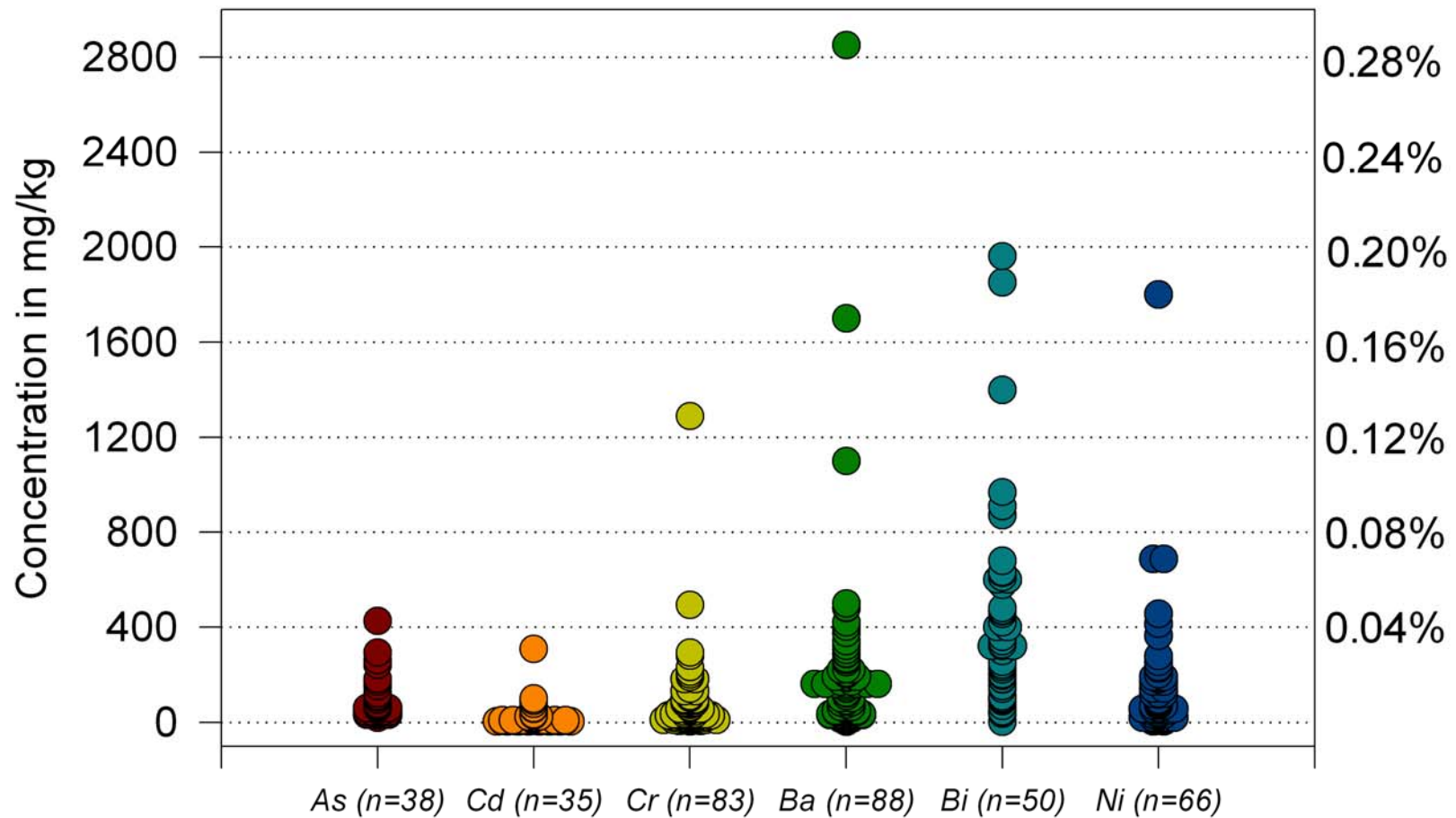
Some Other Interesting "Hits"

Element	City "A" (1) mg/kg	City "A" (2) mg/kg	City "B" mg/kg	City "C" mg/kg	City "D" mg/kg	City "E" Fe mg/kg
Ce	16	8.33	0.7	3.29	2.34	0.28
Co	15	**36.2**	0.2	2.47	6.83	0.69
Dy	3.5	**646**	0.09	**188**	**4450**	**35.9**
Gd	4.5	2.7	0.10	14.1	0.957	0.31
La	19	**38.9**	0.7	1.5	5.62	0.39
Mo	1.3	0.47	< 0.1	8.29	6.48	13.6
Nd	20	**32.8**	0.5	1.33	6.12	0.38
Pr	4.5	7.35	0.1	0.32	1.38	0.09
Rb	< 0.1	0.23	< 0.1	1.14	2.68	0.45
Se	< 1	0.3	1	0.5	7.81	< 0.2
Sm	4.1	6.22	0.1	0.27	1.28	0.07
Tl	0.6	0.38	0.1	12.7	0.24	<0.06
U	1.1	2.66	1.4	**20.4**	8.38	1.47
Y	27	**41.7**	0.5	2.52	6.83	0.36

Why Do We Think This Is Important?

- **Coprecipitation and sorption are potentially *reversible* processes**

- **Dissolution is possible with favorable kinetics**

- **Growth in complexity of health-based water regulations (e.g. Pb, Cu, As, TCR, perchlorate, D/DBP) requires treatment changes**

- **Growth in water demand requires additional water sources, treatment plants, blending**

- **Changes in pressure and flow velocity/direction easily mobilizes sediment and microparticles**

We Already Know That….

- **Many common oxides & oxyhydroxides (especially) are scavengers for trace metals and radionuclides**
  - **Iron oxides and hydroxides are As and U removal media**
  - **Mn compounds oxidize/filter iron, oxyhydroxides remove metals**
  - **Aluminum oxides are sorption media for F, P, V, As**
  - **Abundant literature on metal scavenging by similar solids**
    - **Soil science**
    - **Limnology/stream chemistry**
    - **Geochemistry**
- **Speciation will affect mobility, e.g. V accumulated as sorbed oxyanion vs mineral vanadinite [$Pb_5(VO_4)_3Cl$]**

Conclusions

- **Just about the whole periodic chart potentially can end up on pipes somewhere!**

- **Obviously there is are relationships to**
  - **The source water**
  - **The material itself**
  - **The prior materials passed through**
  - **Treatment process residuals**

- **Formation of mixed solids with pipe metal may alter mobility within premise plumbing or parts of the DS**

- **Not sure what is really mobile and available for human exposure, but POTENTIAL is there**

Conclusions

- **Clear evidence that entry-point monitoring was/is inadequate**
  - To characterize DS conditions
  - Catch exposure problems

- **Solid theoretical basis to expect reactive behavior of various inorganics and radionuclides with pipe materials & scales**

- **"Safe" levels in finished waters could accumulate over time in pipes and be released**
  - Sometimes unpredictably
  - Sometimes at high concentration

Some Points of Concern

- **Indirect reactions** may induce other problems not discernible by entry-point or LCR monitoring
  - Coprecipitation
  - Nitrification
  - Sequestration
  - Demineralization
  - Blending
  - Enhanced disinfection

- **Hydraulic disturbances** can mobilize metals without detection
  - What ELSE is happening when you flush?
  - What happens in mixing zones?

- What happens with polyphosphate "cleaning" programs?

- What else is there during and after "red" and "black" water?

A Question of Balance: Offsetting Factors

- **Deposition on/in scales is not necessarily completely reversible**
  - **Function of speciation**
  - **Function of kinetics**

- **Only a certain fraction of surficial material may be mobile in response to give water chemistry changes**

- **The health risk is generated a complex function of**
  - **physical and background chemistry interactions**
  - **duration/extent of disturbance**

- **Only some water systems may have particular noxious constituents in their raw or finished water**

Precautionary Activities

- **Note that it *may not be chemically possible* to avoid destabilization or release of accumulated metals in some circumstances**

- **Know the locations of materials in DS and how water flow relates to them**

- **Potential changes in water treatment should trigger analysis of impact on scales, and enhanced monitoring during implementation**
  - **Anything that changes pH or redox state of DS water**
  - **Corrosion inhibitors or other shifts in major anionic background**
  - **Coagulation/coagulant changes**
  - **Disinfection/disinfectant changes**
  - **Membrane filtration**
  - **Mixing/blending**

Precautionary Activities

- **Know what inorganics/radionuclides are in source water, even if below MCL**
  - **Monitor periodically in DS**
  - **Trigger more DS monitoring when**
    - **Hydraulic disturbances (fires, main breaks, flushing)**
    - **Drought conditions or storms change water quality**
    - **Unusual microbial data noted**
    - **Consumers complain of discolored water or unusual tastes**
    - **Fluctuations in finished water major parameters**

Research Needs

- **Much more extensive information on trace metal and radionuclide presence *and speciation* on distribution system scales**

- **Better understanding of competitive impact of different metals and anions on reversibility of sorption in pH range of interest**

- **More complete studies on secondary impacts of coagulation, filtration, disinfection, IX, oxidation processes, media based removal processes, and corrosion control changes on trace metal mobility and scale stability**

Acknowledgments

- **Interagency Agreement DW14999901 with the US Geological Survey, Denver (Dr. Stephen A. Wilson) for metals analyses**

- **The numerous utilities and consultants willing to share their pipe samples**

- **Michael K. DeSantis & Andrea Burkes, Pegasus Technical Services, for photography, additional sample preparation, and supplemental analyses of total C, TIC and S**

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