Examination of the Occurrence of Heavy Metals in Corrosion Scales and Sediments

AwwaRF Project 3118

Gregory V. Korshin and Ching-Yu Peng
Department of Civil and Environmental Engineering
University of Washington, Seattle WA
korshin@u.washington.edu

Outline of the presentation

- Goals
- Analyte groupings
- Analytical methods
- Occurrence
  - Morphology and structure
  - Concentrations
- Release of heavy metals
- Conclusions and research needs

Goals

- Determine the occurrence of representative heavy metals in corrosion scales
- Examine associations between concentrations of inorganic contaminants and common constituents of corrosion scales
- Examine whether the inorganic contaminants are associated preferentially with the mobile part of corrosion solids
  - Hydrant flush solids as a representative groups
- Generate initial data concerning the release of constituents of corrosion scales

Analytical targets (analytes)

- Commonly occurring elements
  - Iron, manganese
  - Phosphorus, sulfur, carbon (organic and inorganic), (silicon)
  - Calcium, magnesium, aluminum
  - Zinc
- Inorganic contaminants
  - Antimony, arsenic, selenium
  - Cadmium, thallium, uranium
  - Nickel, chromium, vanadium
  - Barium, lead, (zinc)

Number and types of samples

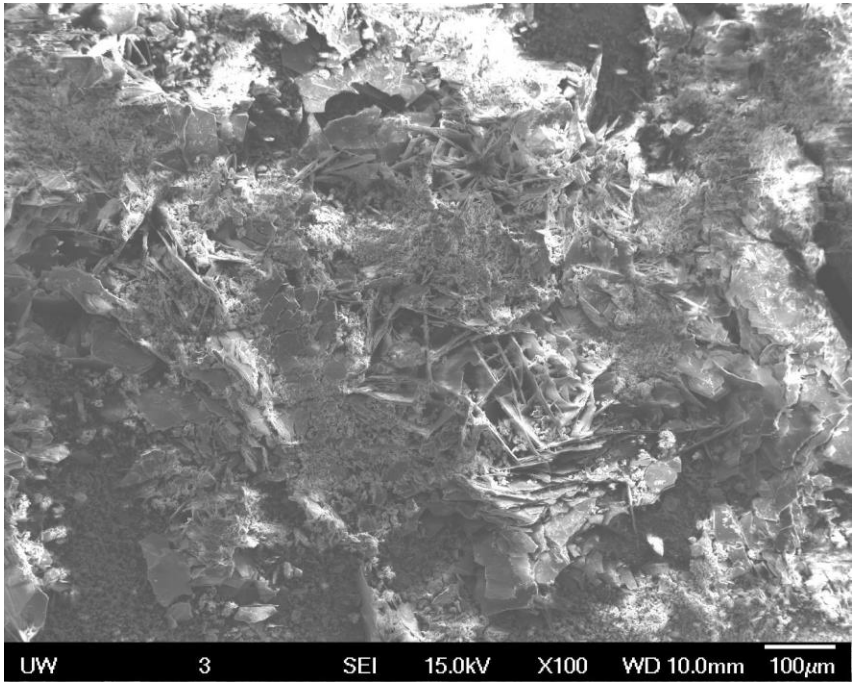
- All samples of solid phases (N=58)
- Hydrant flush samples (N=23)
- All pipe specimens (N=35)
  - Live samples (N=25)
  - Galvanized pipe samples (N=4)
  - All other live samples (N=21)
  - Boneyard samples (N=10)
- Grab water samples

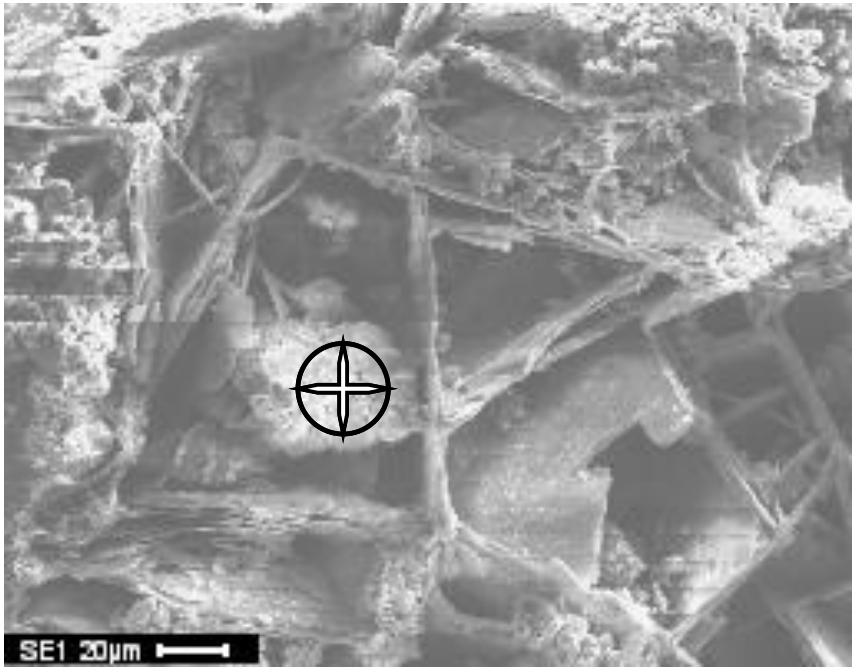
Analytical methods

- ICP/MS analyses for all elements of interest
  - Digestions at University of Iowa (Prof. Valentine's group)
- Perkin-Elmer DRC-e Elan ICP/MS instrument
- Extensive QA/QC procedures
  - SRM 2782 Industrial Sludge
  - SLRS-4 River Water Reference Material for Trace Metals
  - Known additions
  - Internal standards (^{45}Sc, ^{74}Ge, and ^{103}Rh)
- SEM/EDX analyses with a JEOL 7000F high-resolution microscope
- XRD analyses with a Philips PW1830 and Siemens D5000 diffractometers

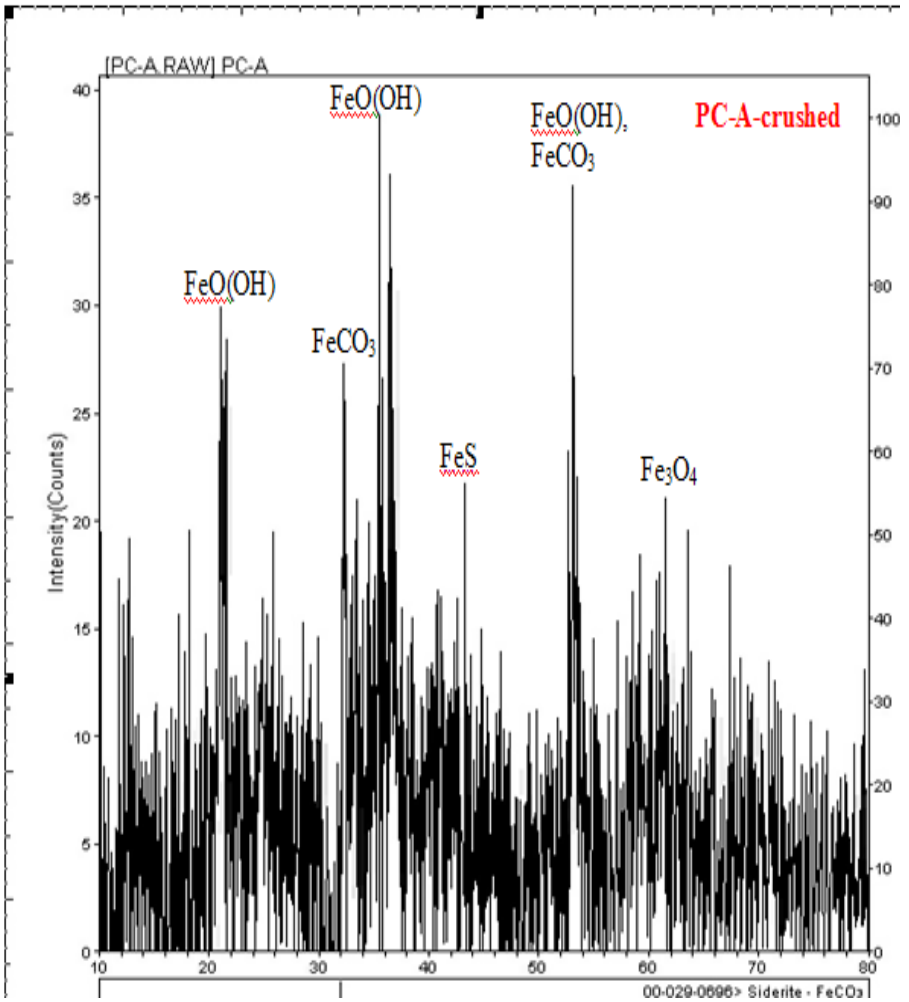
Typical visual appearance of corrosion solids (average digestion yield about 90%)

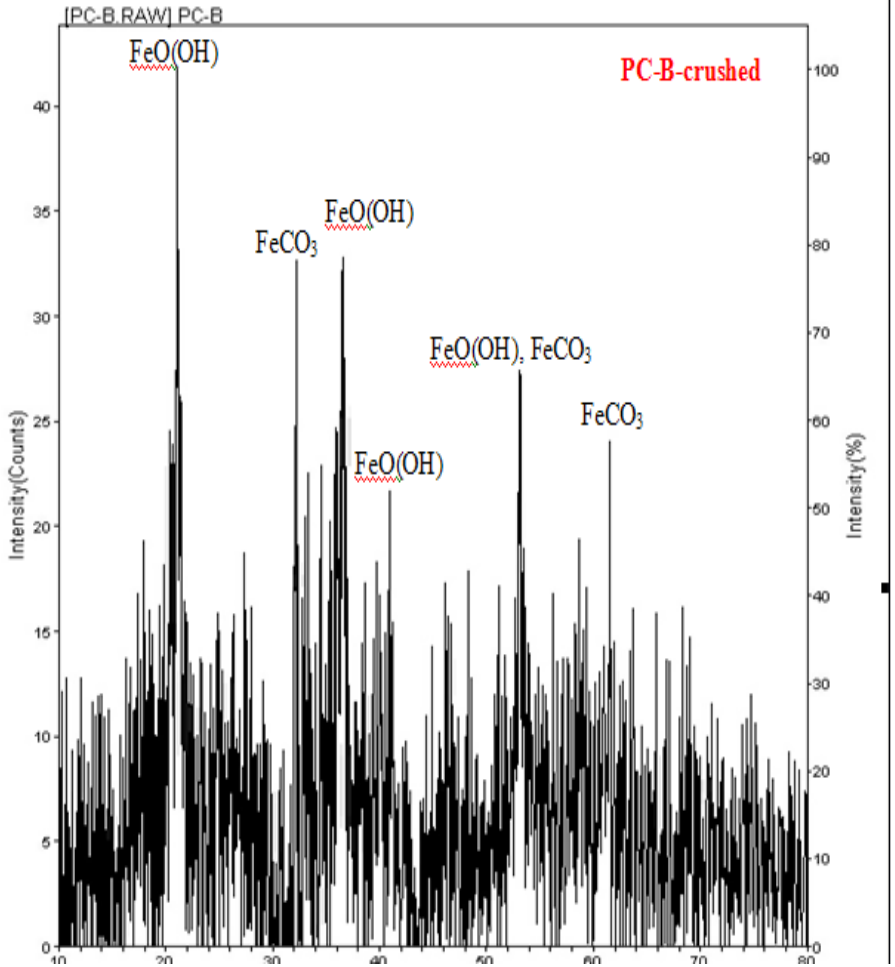
SEM and XRD data for a sample of galvanized pipe solids



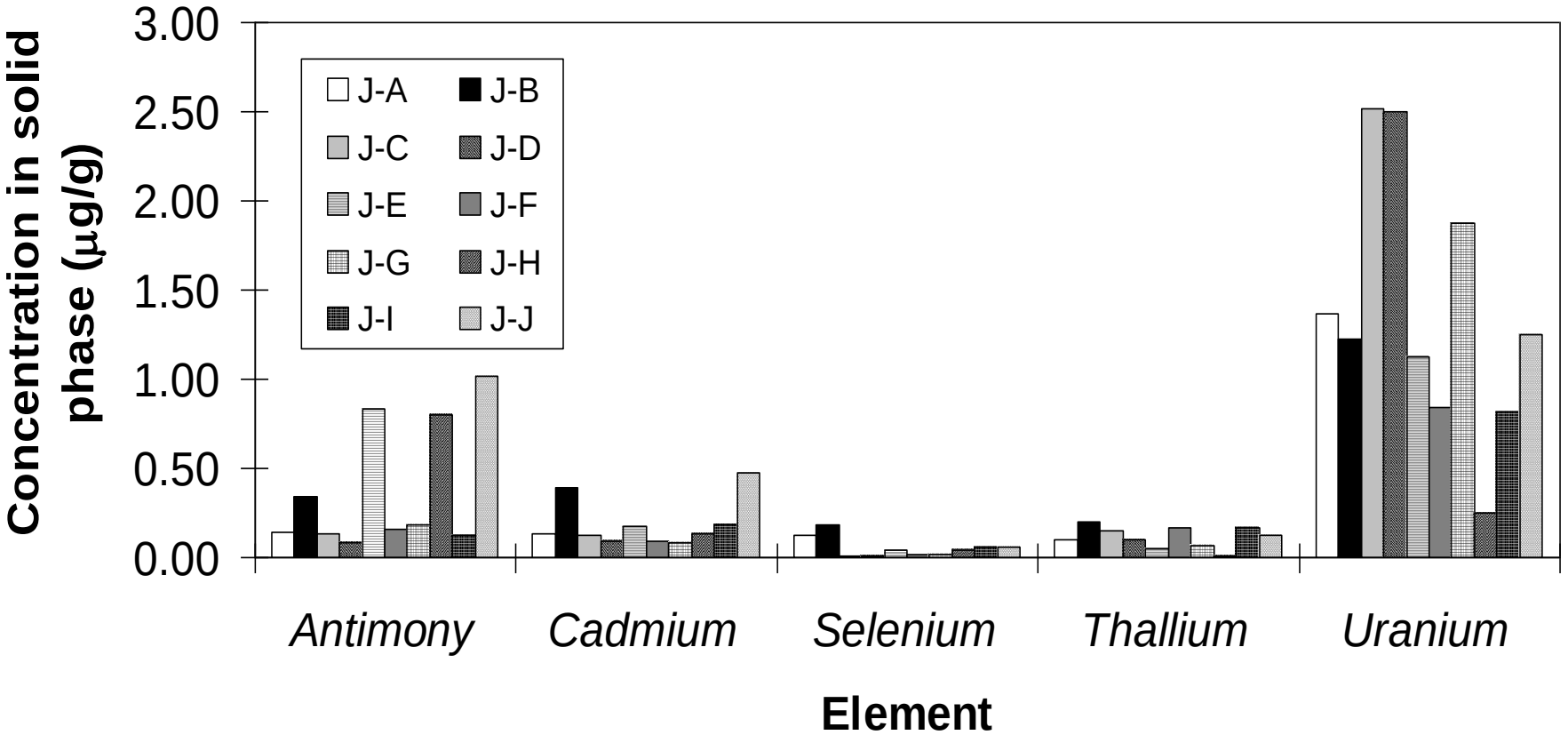


XRD data for galvanized pipe solids

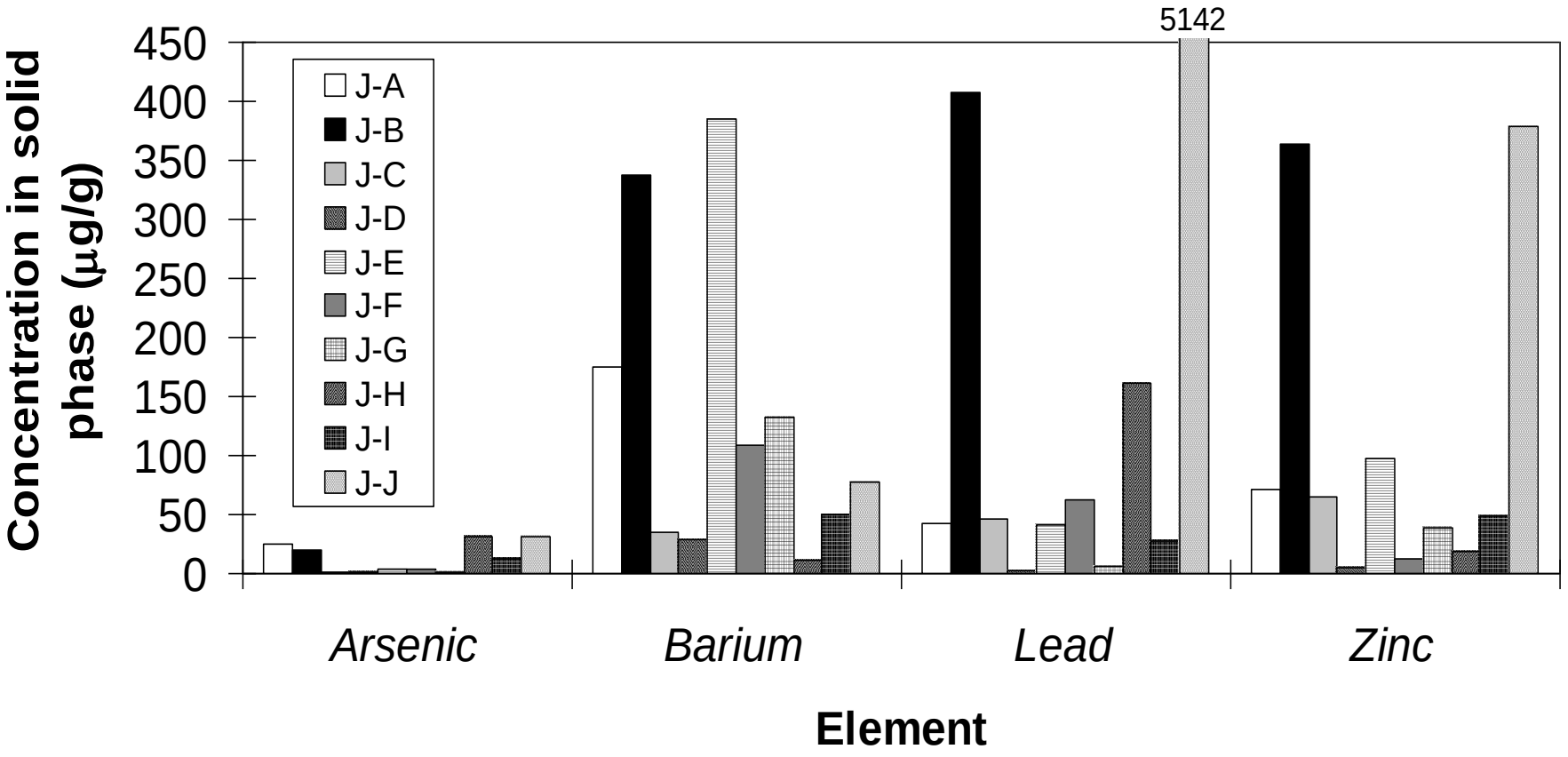




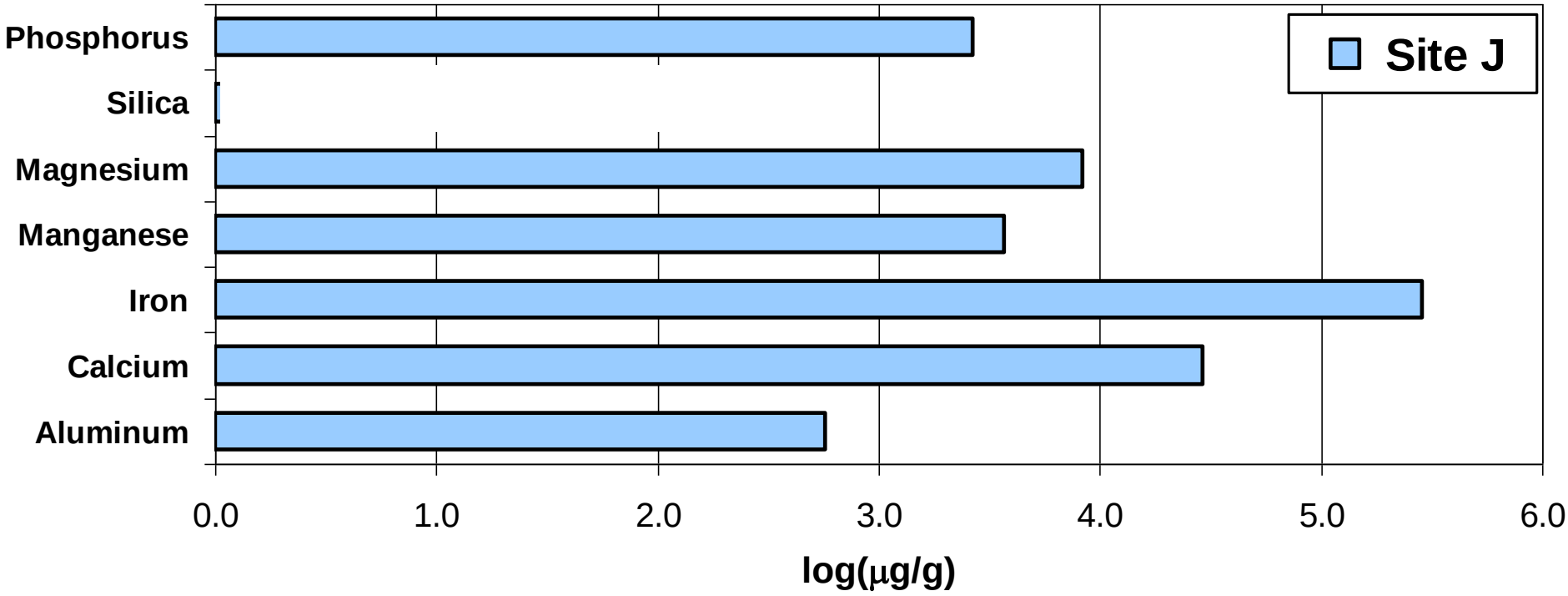
Site J samples: inorganic contaminants in hydrant flush solids



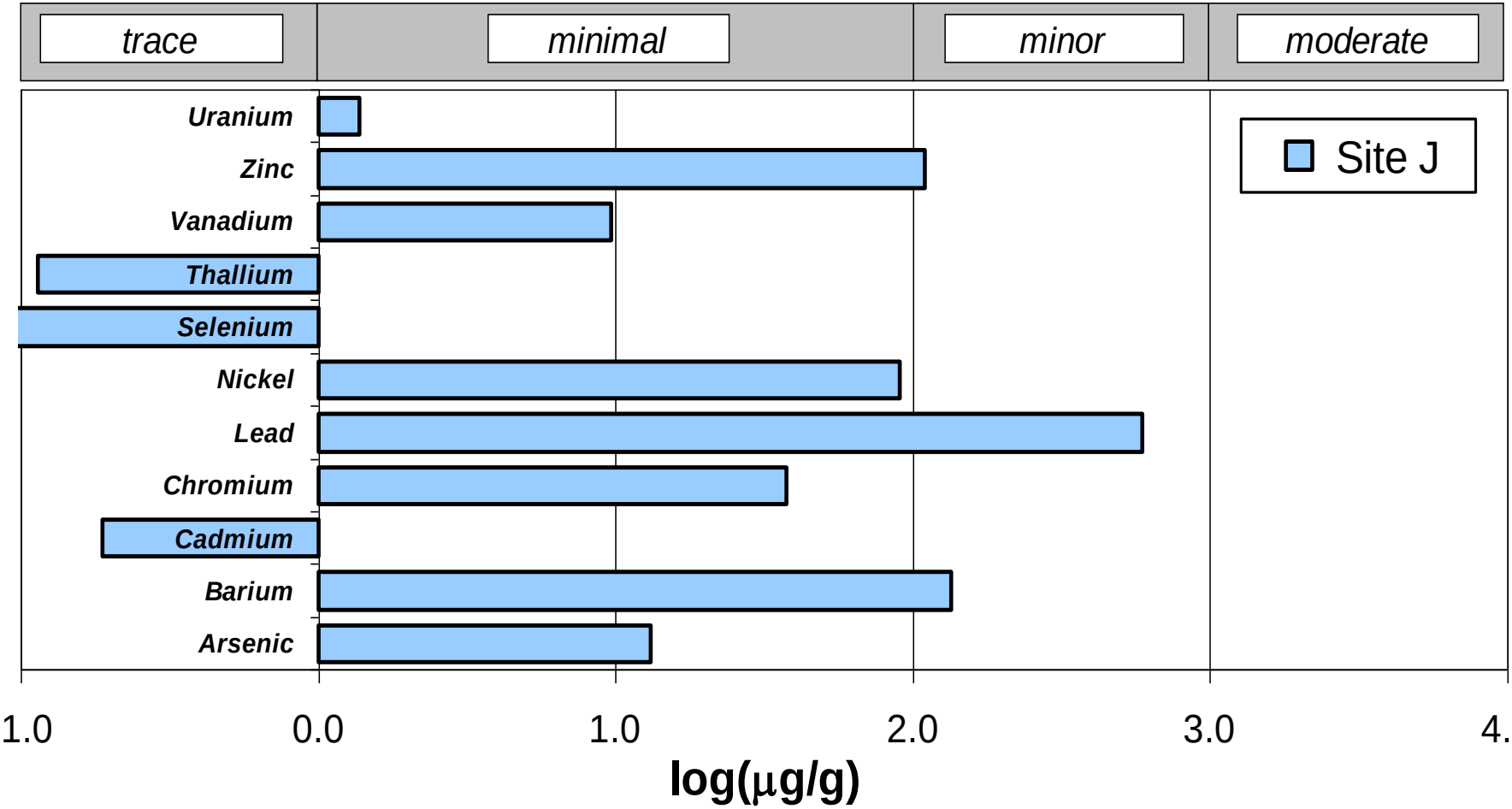
Site J samples: inorganic contaminants in hydrant flush solids



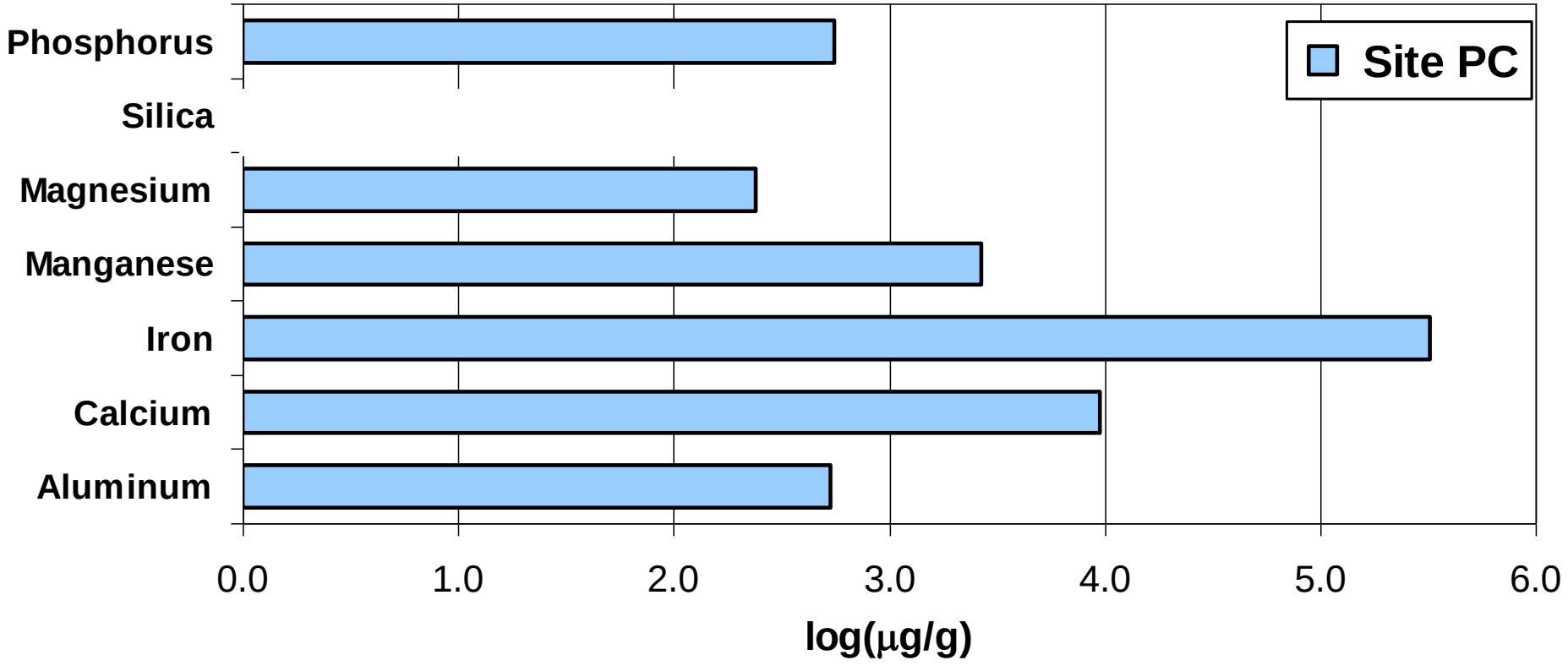
Average levels of commonly occurring elements, hydrant flush solids



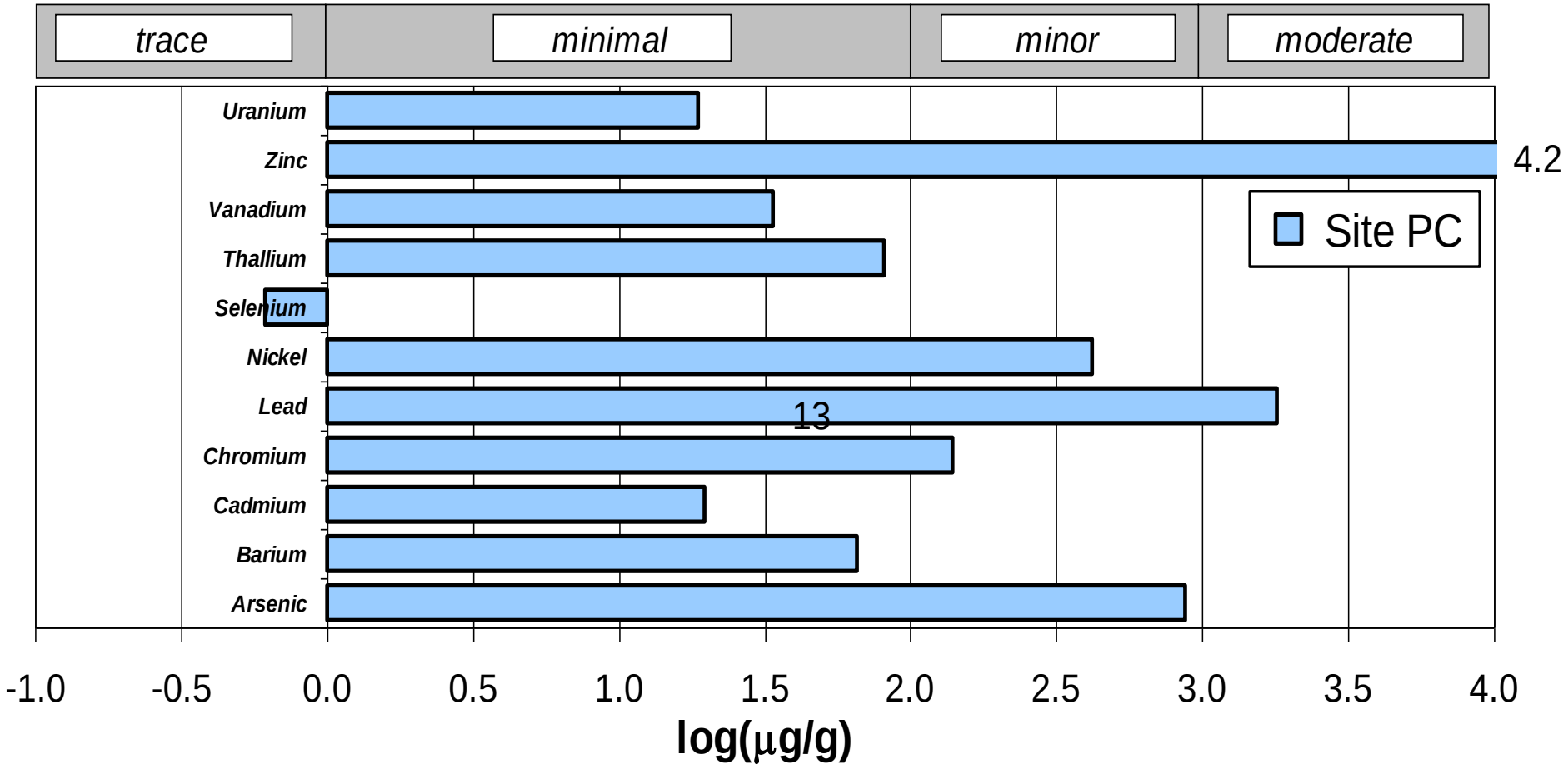
Average levels of inorganic contaminants, hydrant flush solids



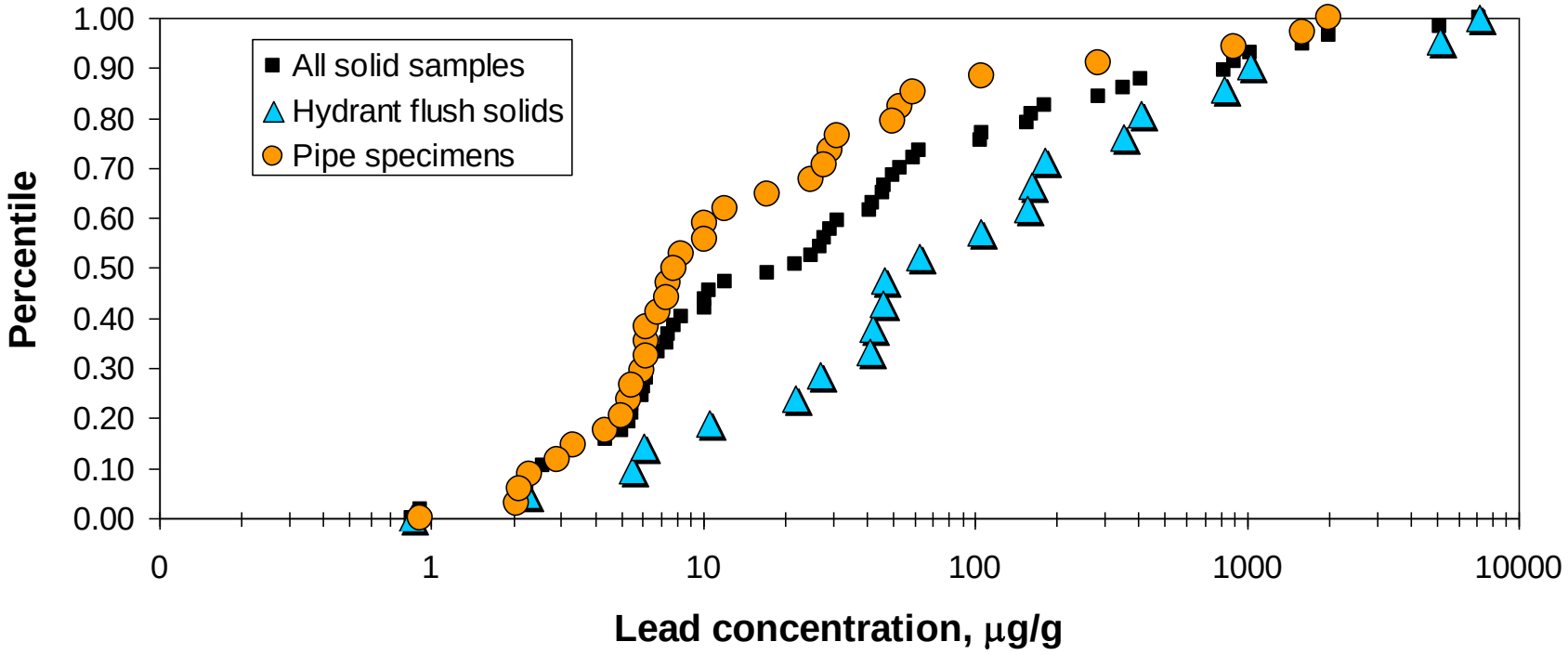
Average levels of commonly occurring elements, galvanized pipe solids



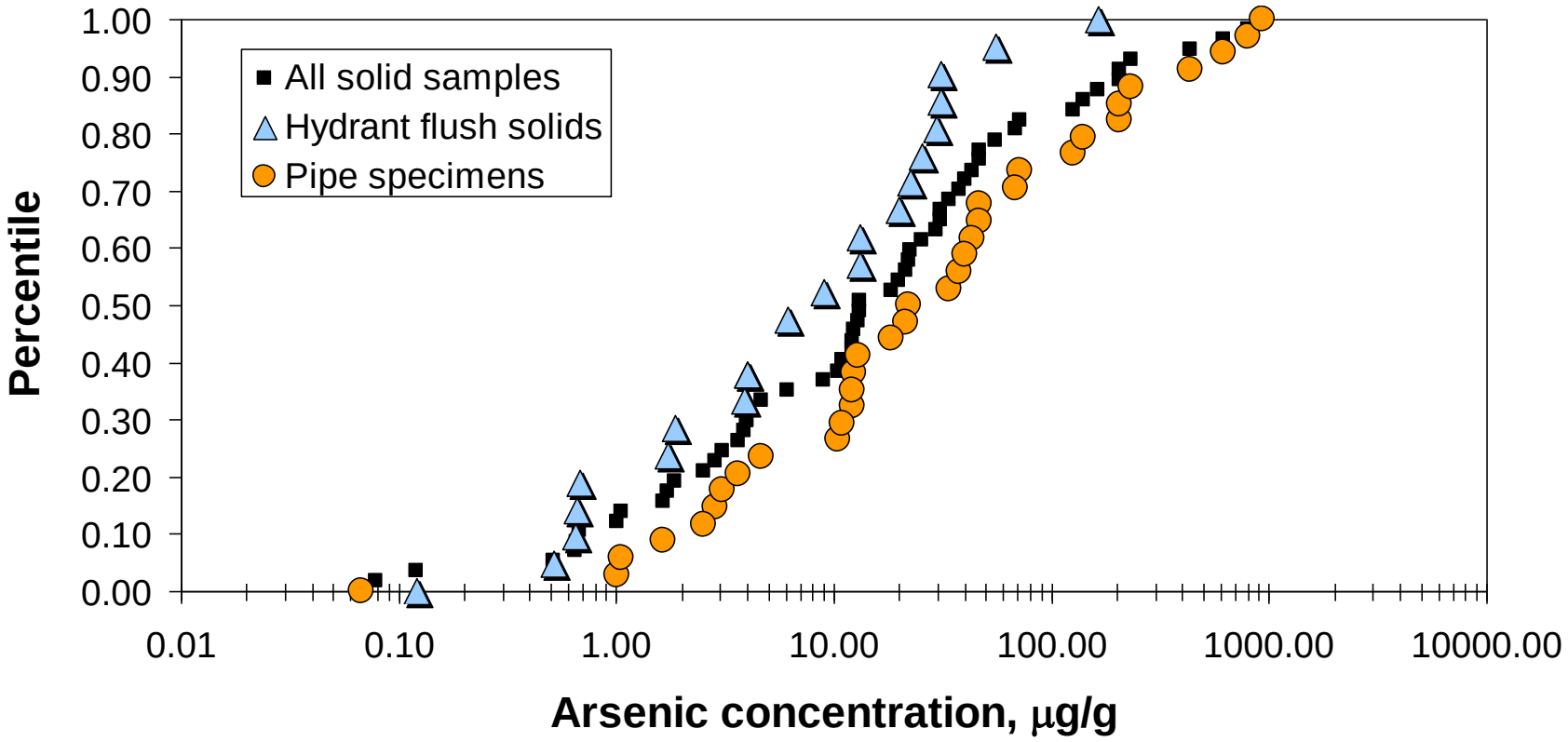
Average levels of inorganic contaminants, galvanized pipe solids



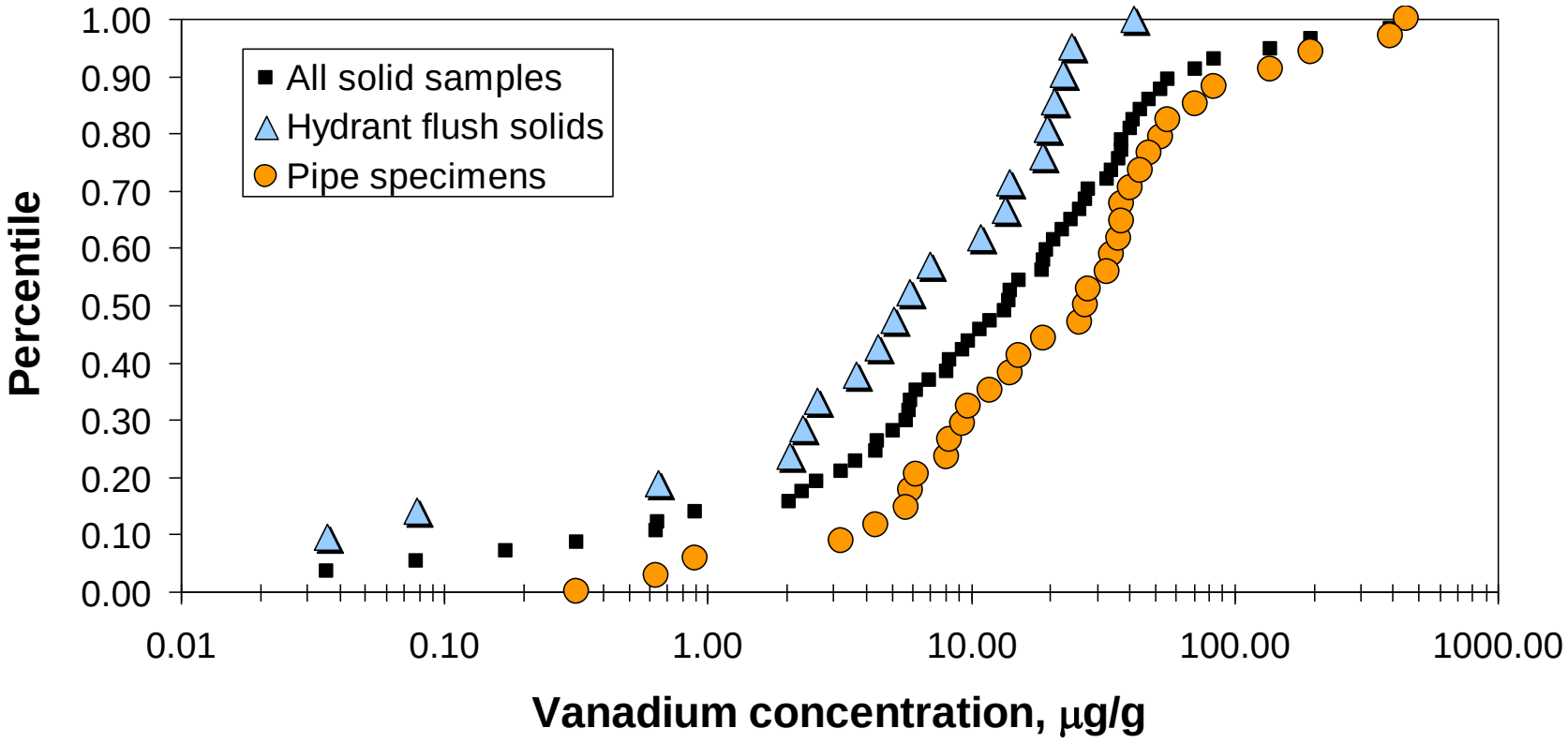
Distribution of lead concentrations in solid samples



Distribution of arsenic concentrations in solid samples



Distribution of vanadium concentrations in solid samples

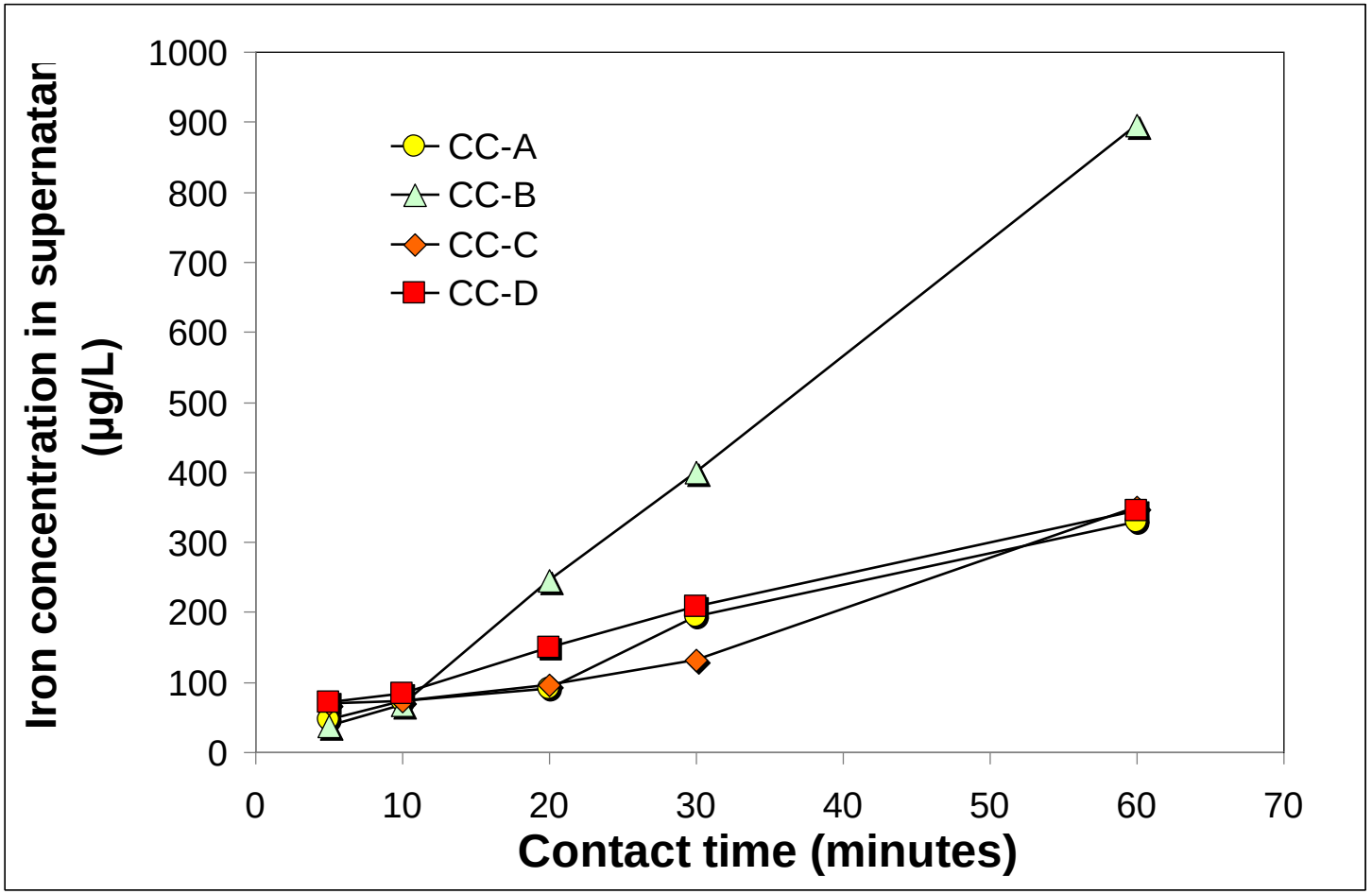


Examination of release of heavy metals from corrosion deposits

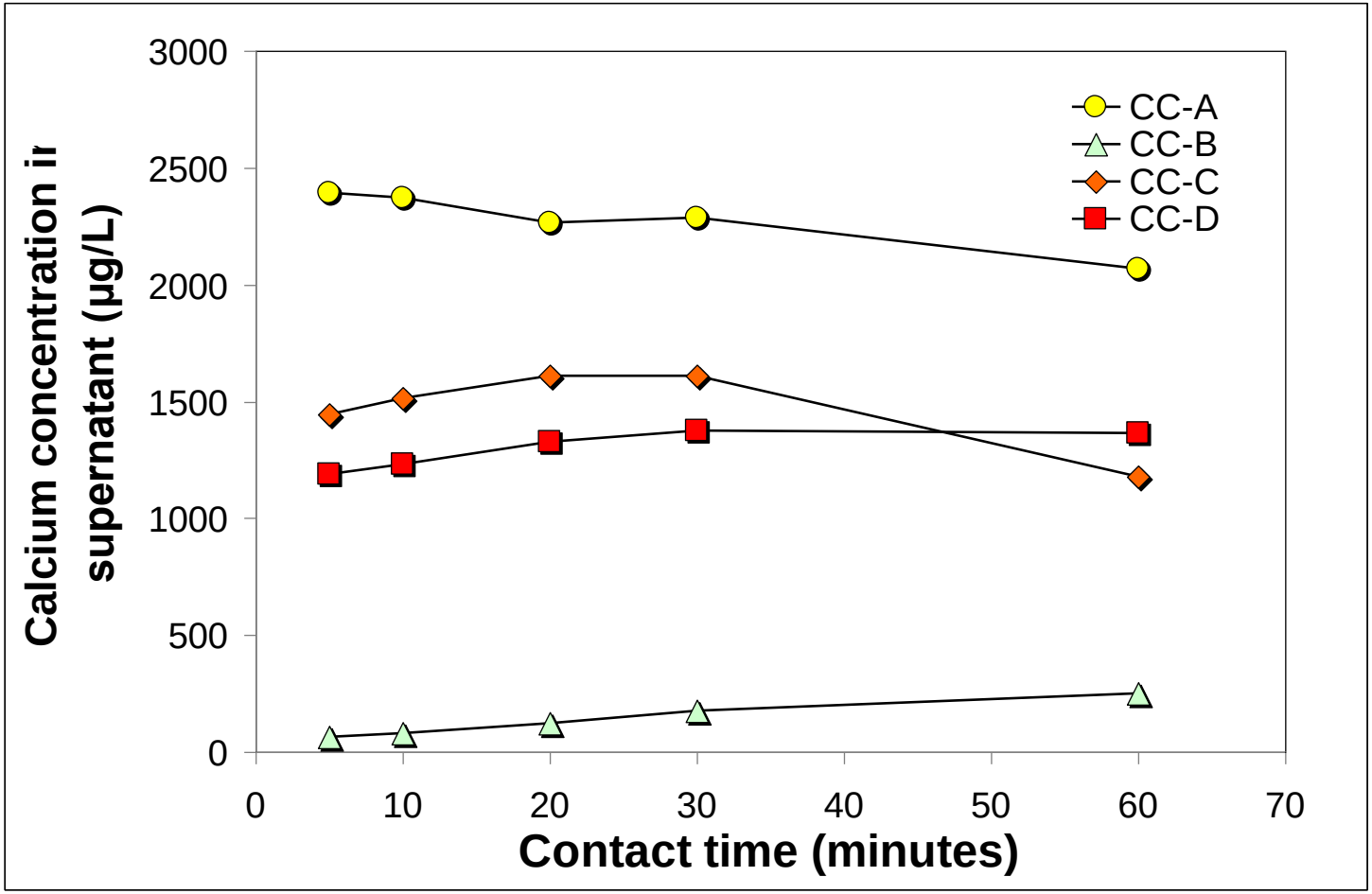
System Identifier	Sample Identifier	Piping Material	Sample Type	Chromium	Vanadium	Lead	Nickel	Arsenic
G	CC-A	UCI	Boneyard Pipe Sp	7	196	60	121	40
G	CC-B	UCI	Boneyard Pipe Sp	29	71	10	93	234
G	CC-C	UCI	Boneyard Pipe Sp	117	36	106	250	620
G	CC-D	UCI	Boneyard Pipe Sp	79	37	17	296	140

- **Methodology**
  - Suspension of 1.5 g solid per 1 L
  - pH 7.5
  - Alk. 120 mg/L
  - Varying contact times
- **Analyses for soluble metals**

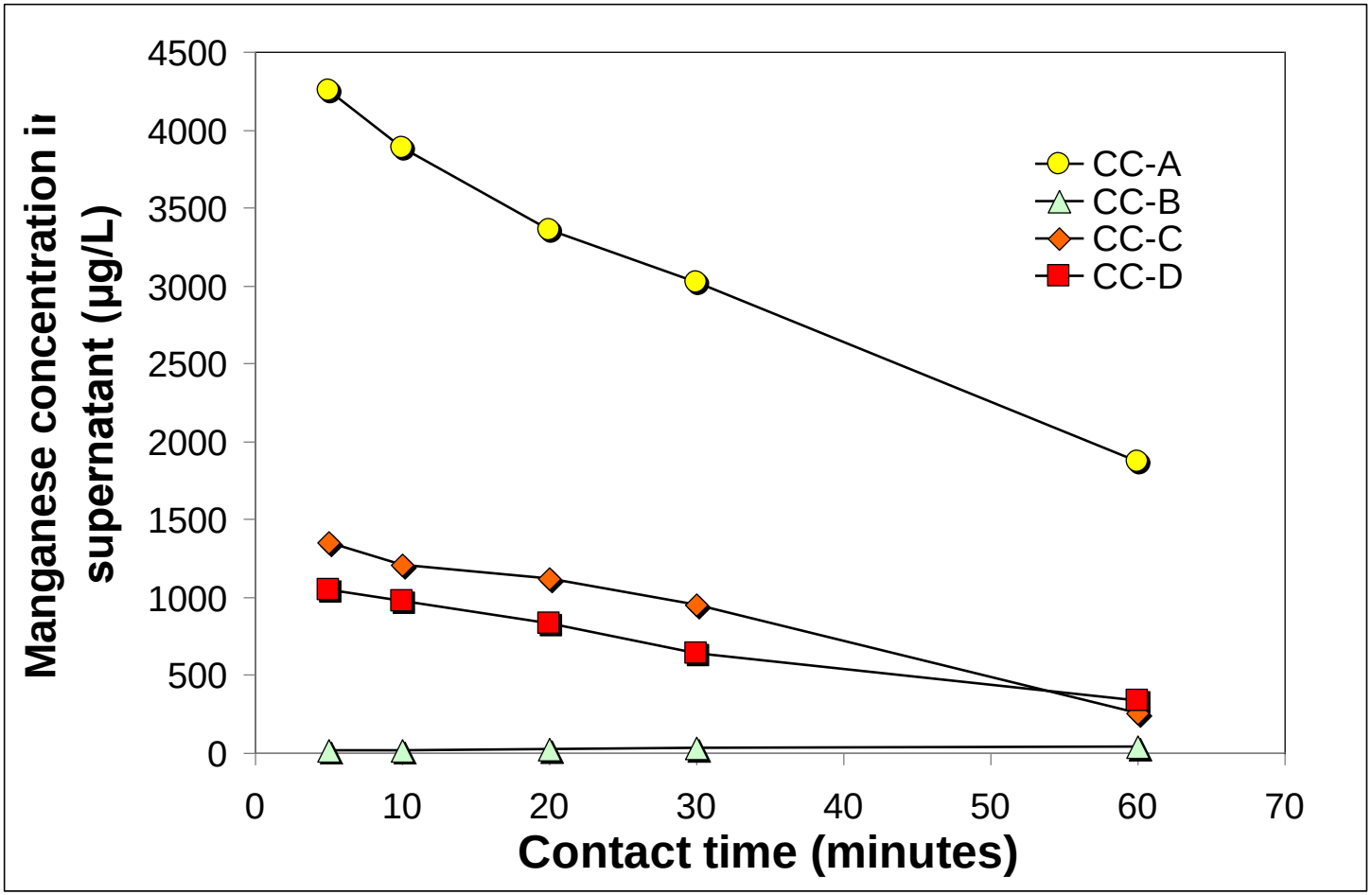
Time profile of iron release from selected samples



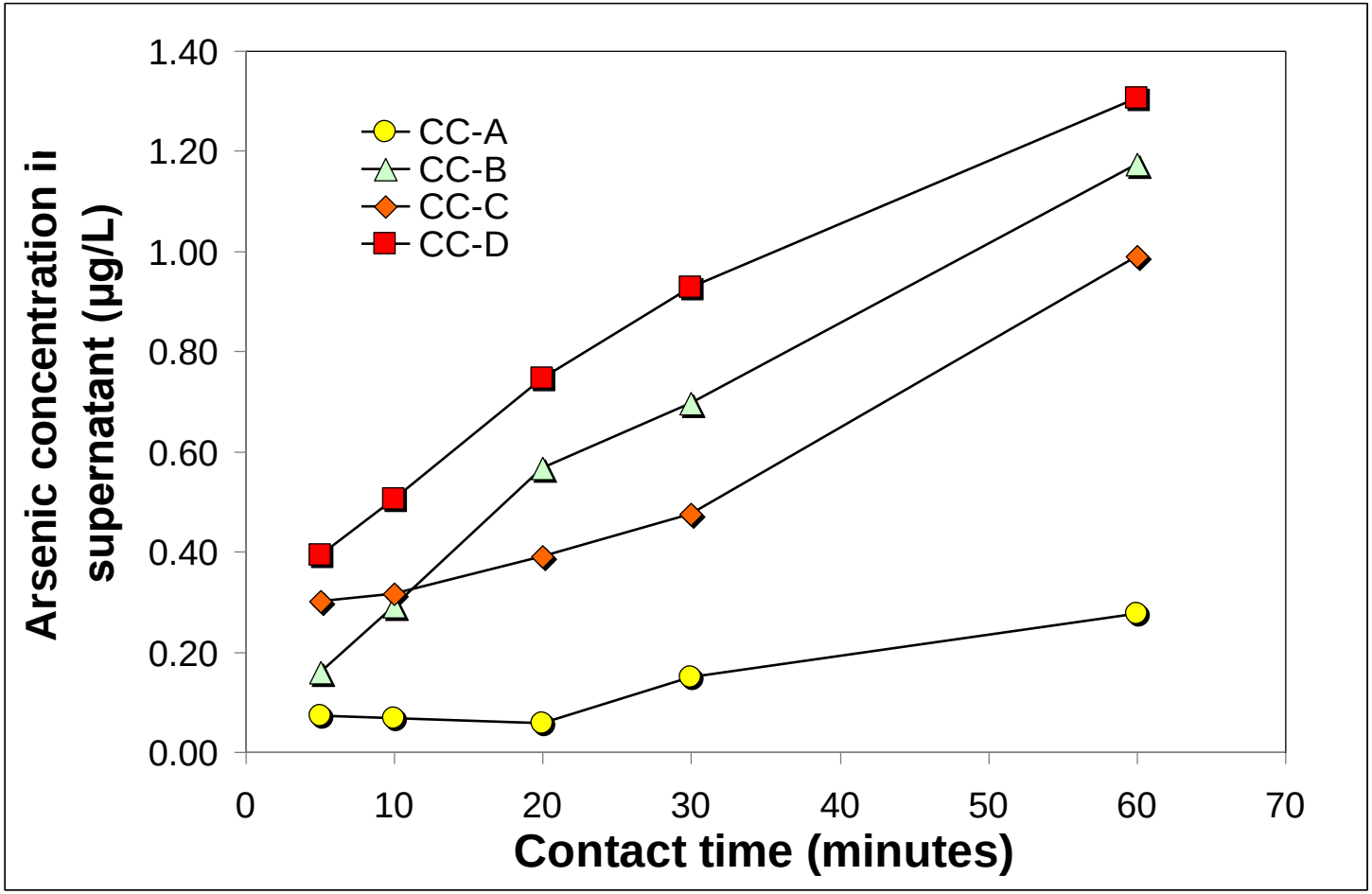
Time profile of calcium release from selected samples



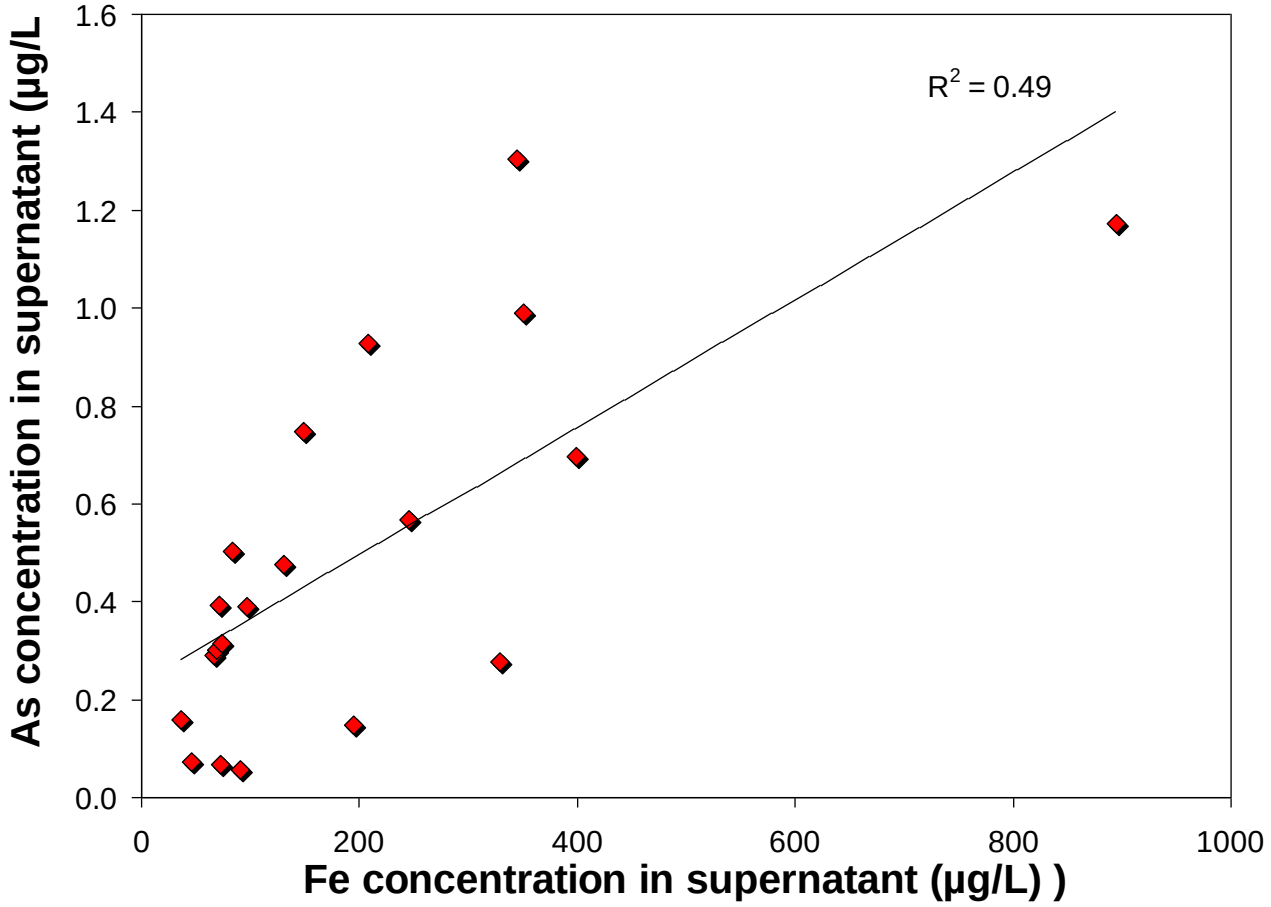
Time profile of manganese release from selected samples



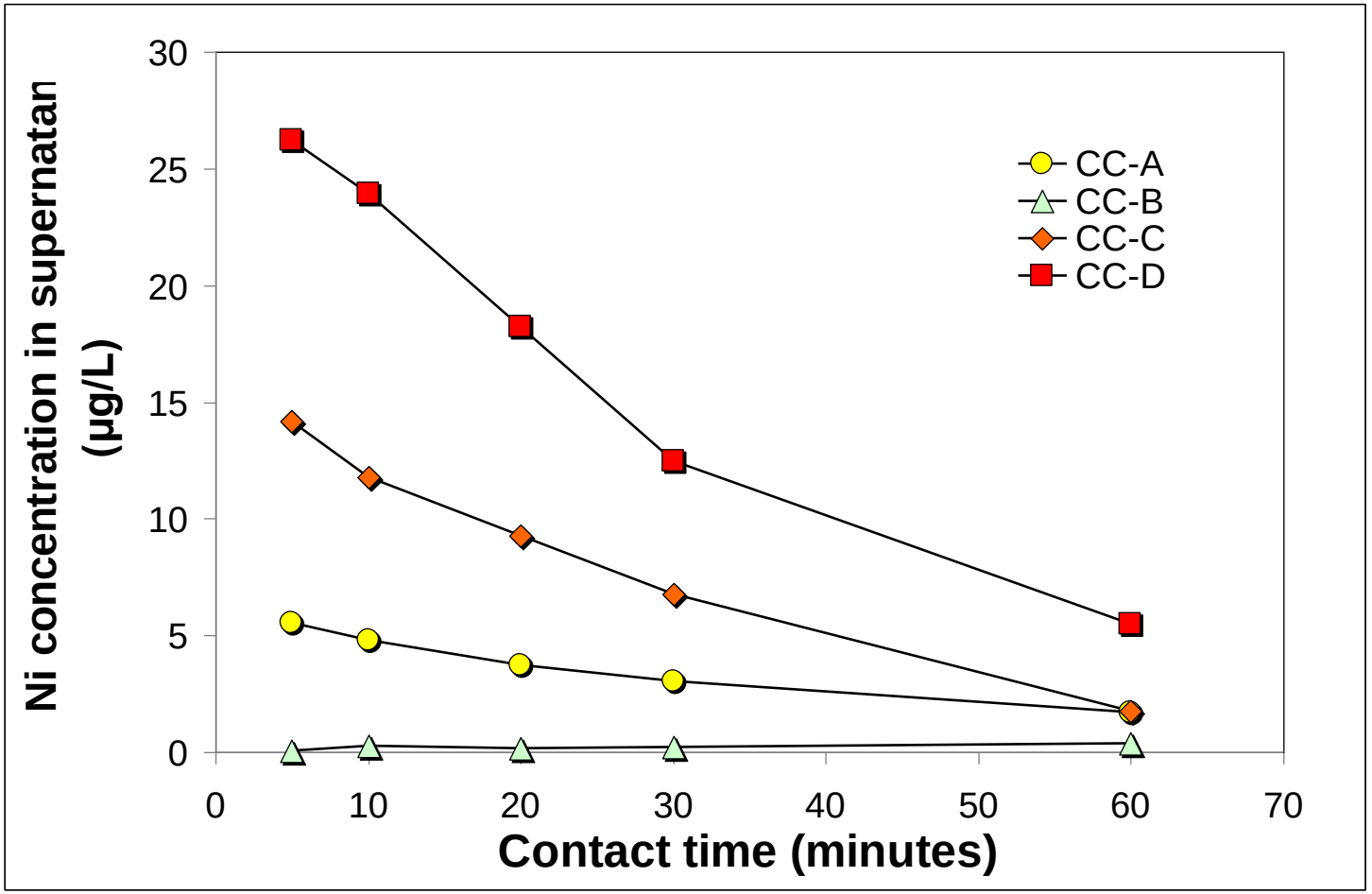
Time profile of arsenic release from selected samples



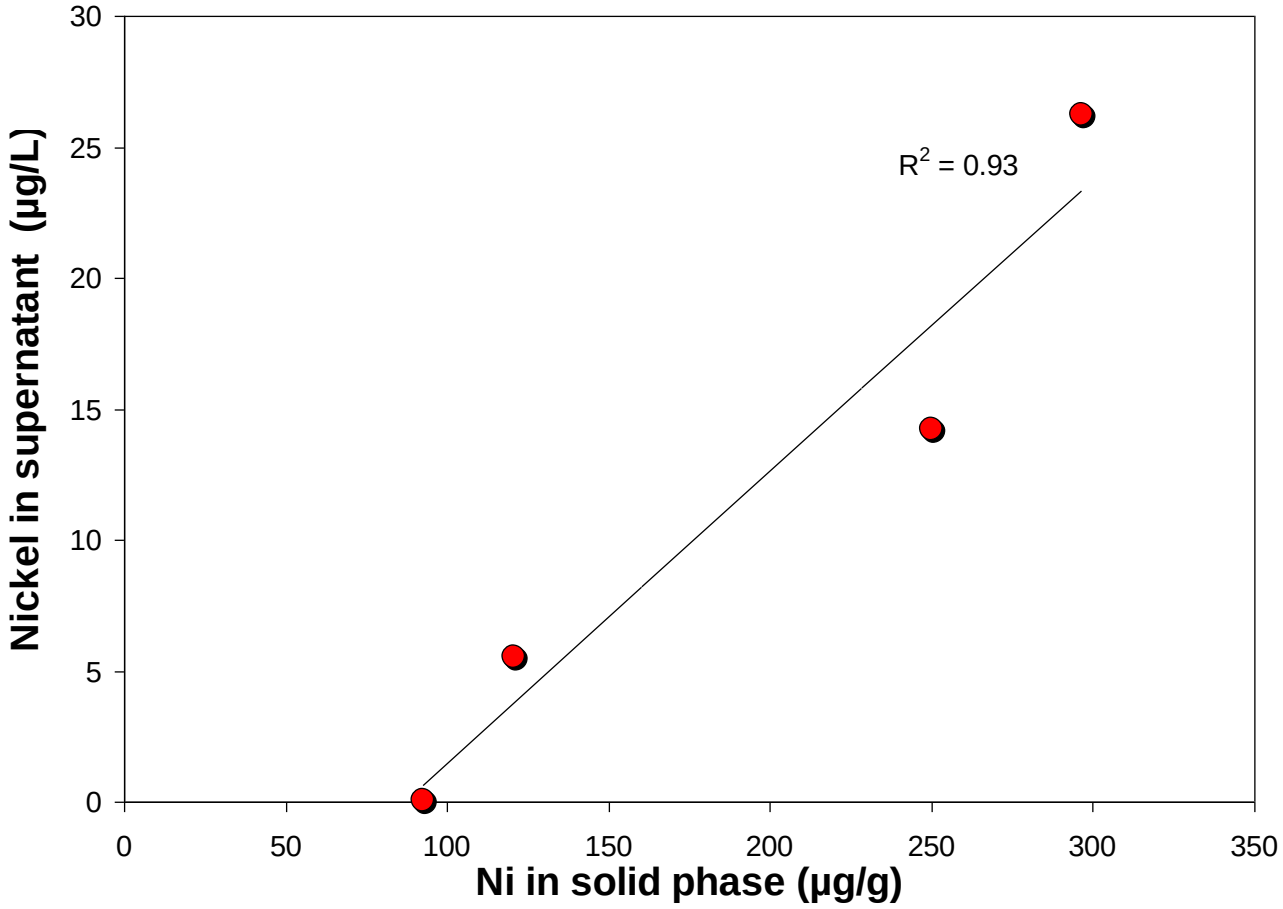
Correlation between arsenic and iron release from selected samples



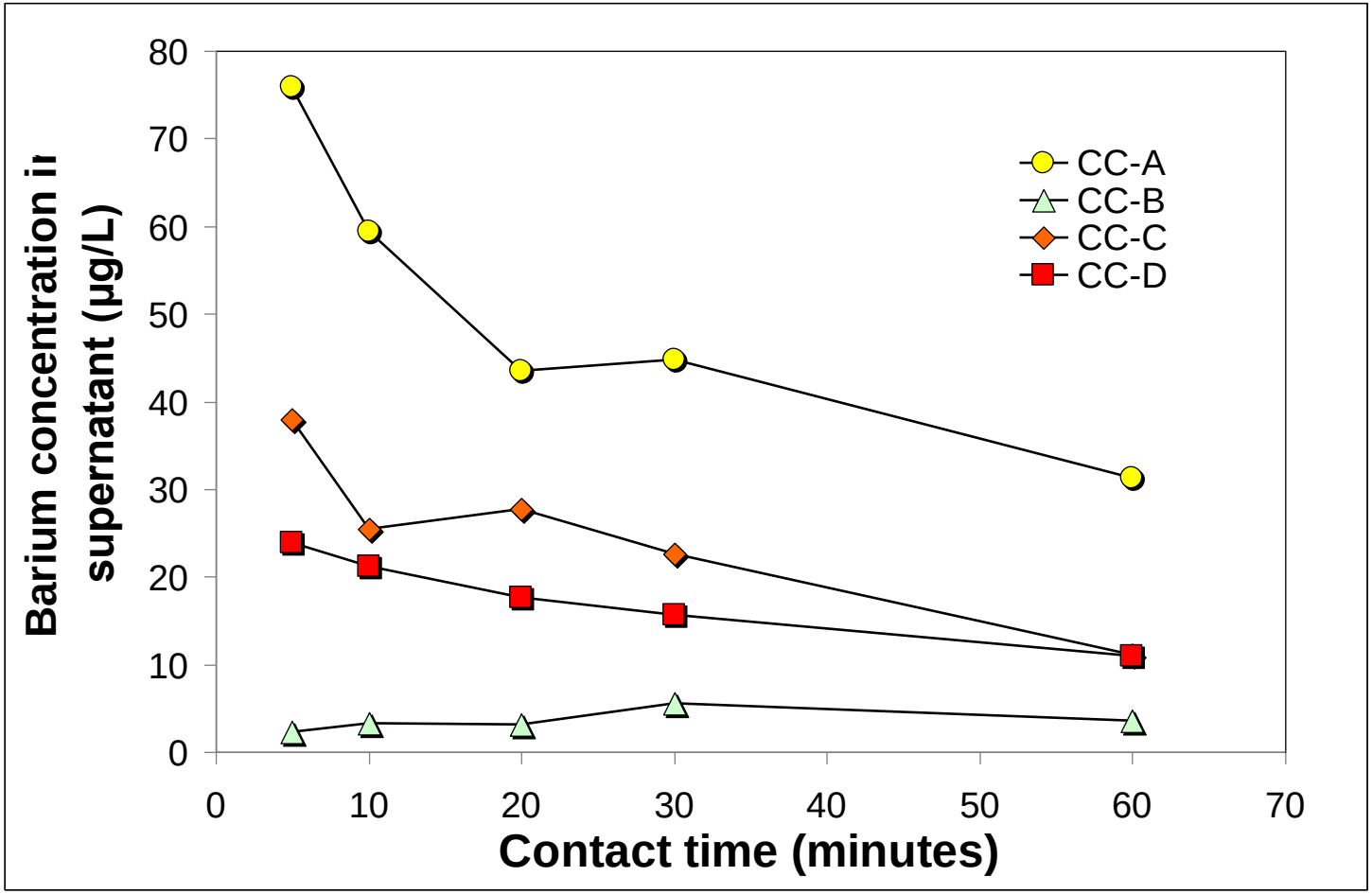
Time profile of nickel release from selected samples



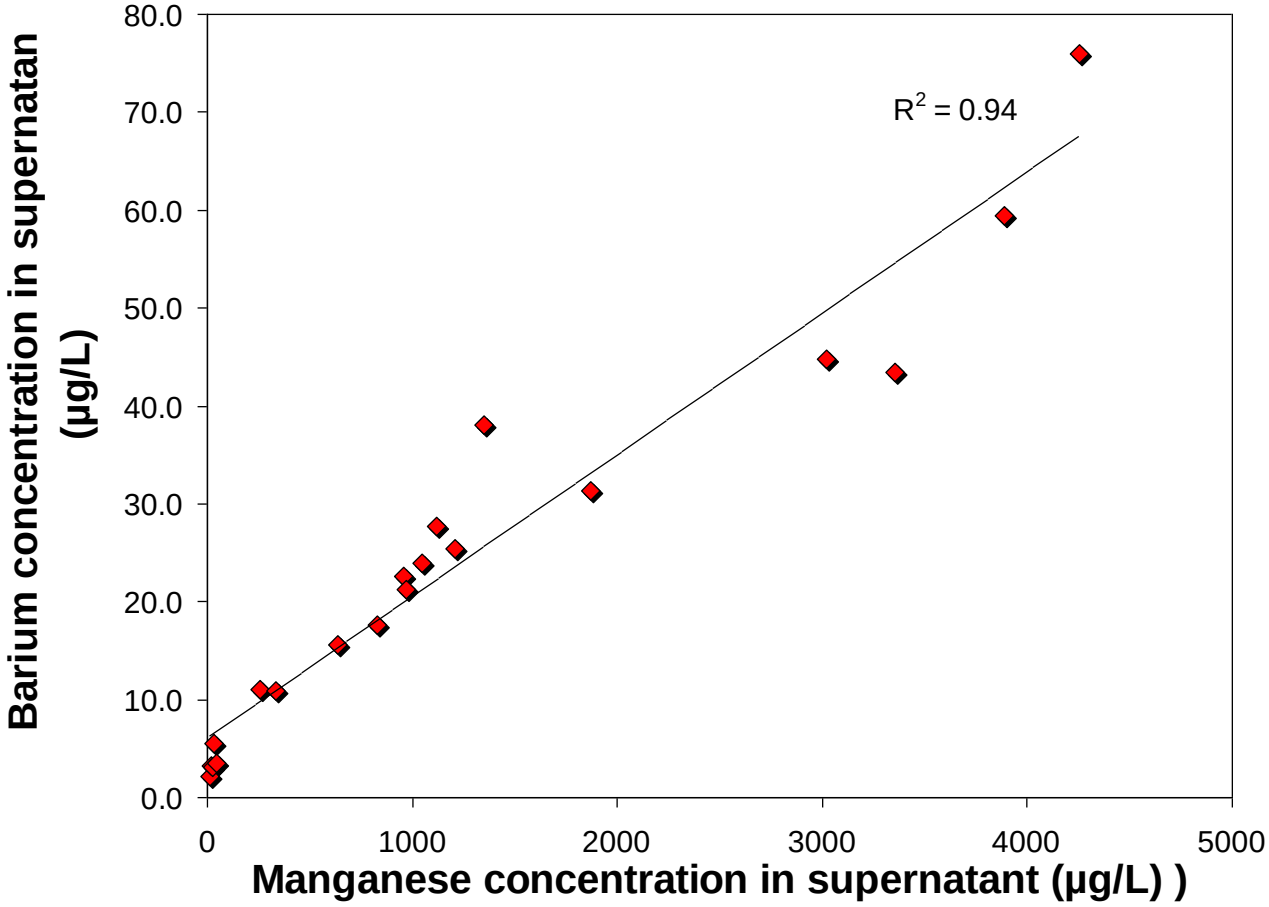
Correlation between Ni release and Ni concentration in corrosion scales



Time profile of barium release from selected samples



Correlation between barium and manganese release



Conclusions –inorganic contaminants

- All hydrant flush solids and pipe specimens are highly complex morphologically and structurally
- A wide range of heavy metals have been found in them
- Their concentrations change dramatically from one site to another and within each site

Conclusions –inorganic contaminants

- Antimony, cadmium, selenium, thallium and uranium occurred at trace levels.
- Arsenic, nickel, chromium and vanadium tend to occur at minimal concentrations.
  - Concentrations were elevated in galvanized pipe samples.
- Release of major components of scales and heavy metals follow complex mechanisms
  - Monotonic increase with time for Fe and As.
  - Very rapid increase followed by gradual re-sorption for Ni, Ba and Mn

Future research needs

- Mechanisms of accumulation of inorganic contaminants in corrosion scales and sediments remain to be ascertained
- Factors that affect the variability of concentrations inorganic contaminants in solid samples in each site remain to be determined.
- All aspects of release of inorganic contaminants from corrosion scales and potential exposures to them remain to be studied.

Acknowledgments

- Awwa Research Foundation
- Project team
  - Andy Hill and Steve Reiber (HDR)
  - Melinda Friedman (Confluence Engineering)
  - Prof. Richard Valentine (University of Iowa)
- Many colleagues and students at the University of Washington

Accumulation of trace-level inorganic contaminants in corrosion scales and sediments

- Many drinking water distribution systems have operated for many dozens of years
- During that time, most systems have accumulated massive amount of corrosion scales and sediments
- Many solids, notably Fe- and Mn- oxides, hydroxides and mixed phases are highly active towards sorbing trace-levels inorganic species and radionuclides
  - from vanadium to uranium