Monitored Natural Attenuation Demonstrations for Coal Combustion Residuals Constituents in Groundwater

ANCHOR QEA

Presented by

Jim Redwine, Dimitri Vlassopoulos, Kristi Mitchell, Minna Carey, and Masa Kanematsu

August 9, 2022

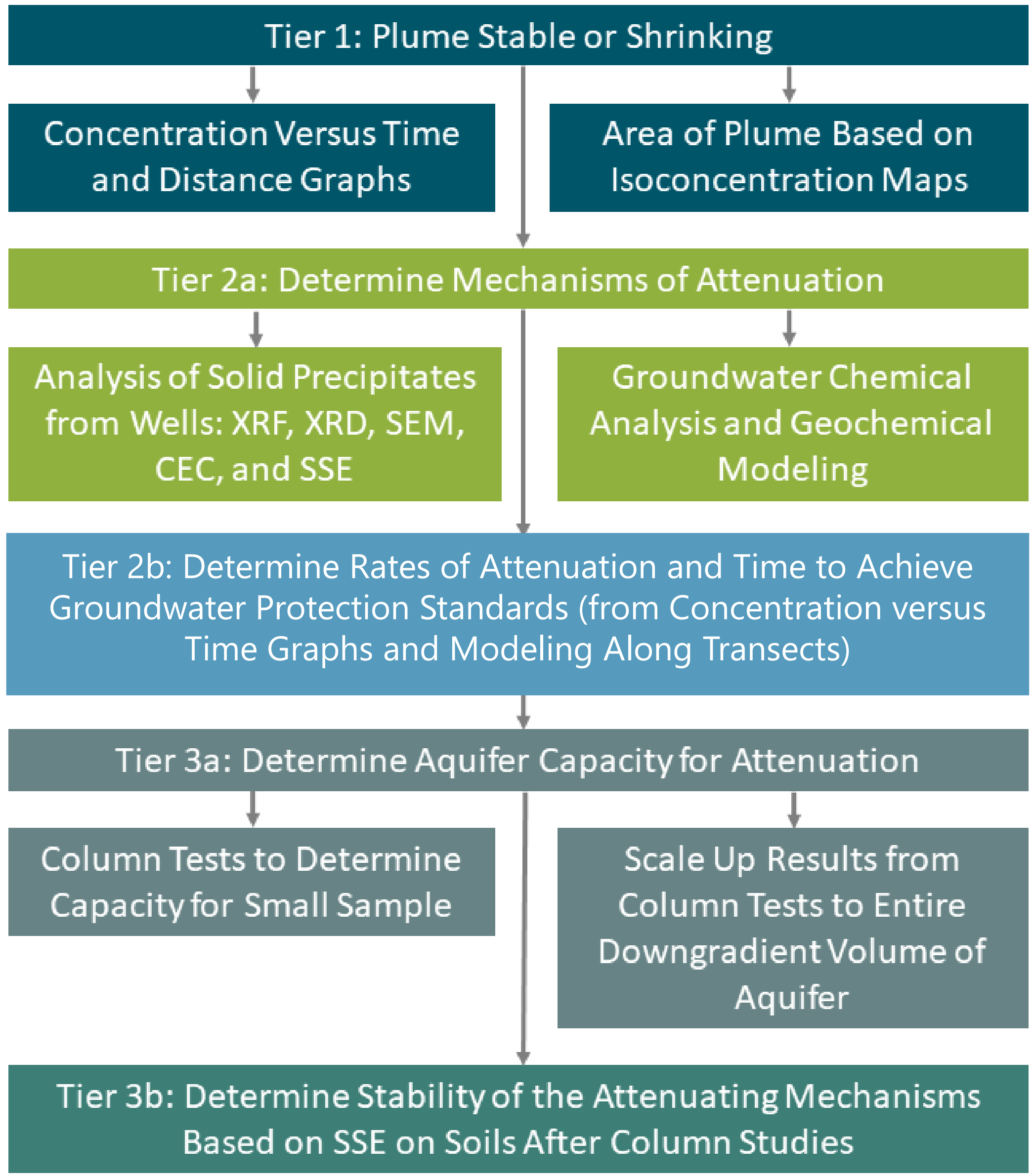
Monitored Natural Attenuation (MNA) Observations

- Definition: Natural processes to achieve groundwater protection standards within a reasonable time frame as compared to other remedies; carefully monitored
- Natural attenuation for coal combustion residuals (CCR) constituents will be operating to some degree at all CCR sites
- Not a default or do-nothing technology; requires rigorous science to document and monitor for effectiveness
- Often one part of an overall site corrective action strategy, combined with other remedies
- Allows more aggressive remedies to be focused in areas of greatest need, thereby increasing efficiency and reducing cost

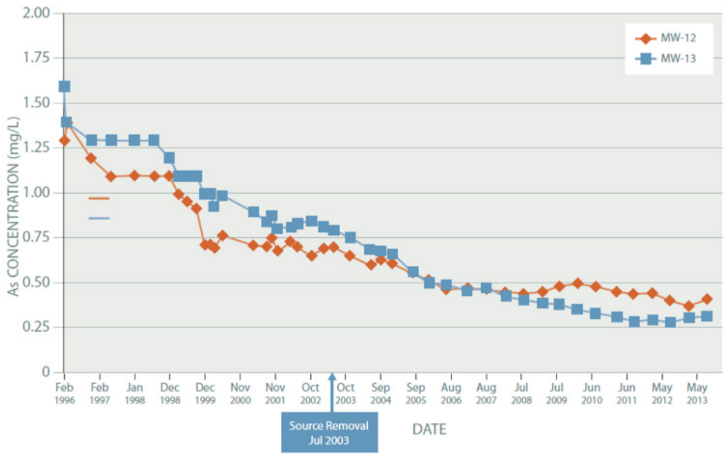
Four Phases or Tiers of MNA

- Tier 1: Demonstrate area of impacts (plume) stable or shrinking
- Tier 2: Determine mechanisms and rates of attenuation
- Tier 3: Determine system capacity and stability of attenuated constituents
- Tier 4: Design a performance monitoring program and identify alternate remedies should MNA not achieve groundwater protection standards in a reasonable time frame (adaptive site management)
- Sources: USEPA 1995, 2015

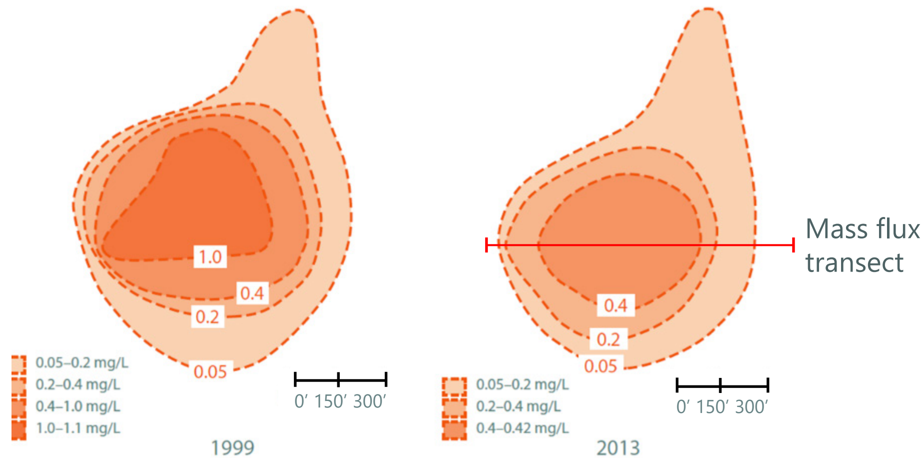
MNA Evaluation Process



Tier 1: Plume Stable or Shrinking

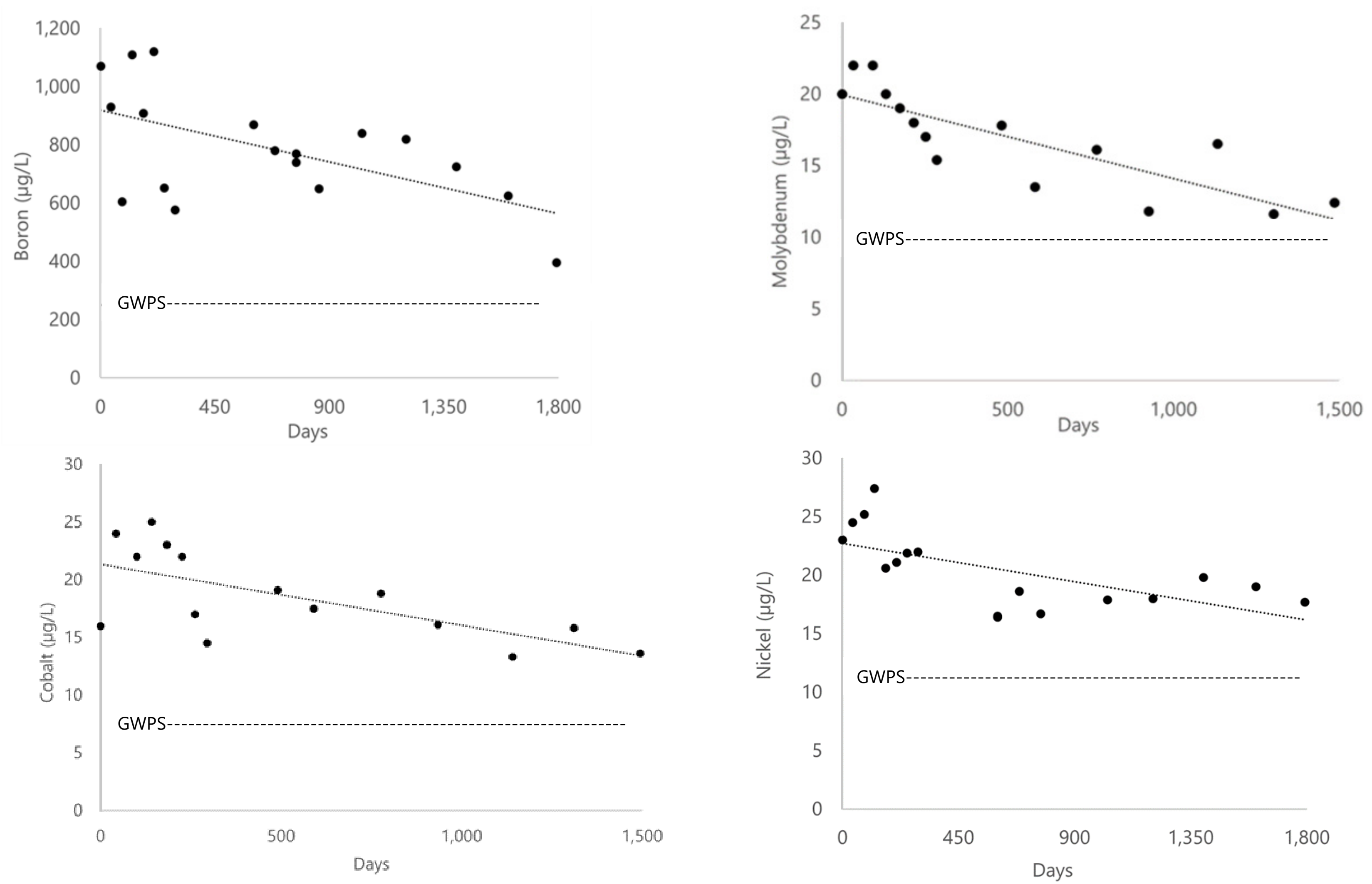


Decrease in arsenic through time in wells 12 and 13

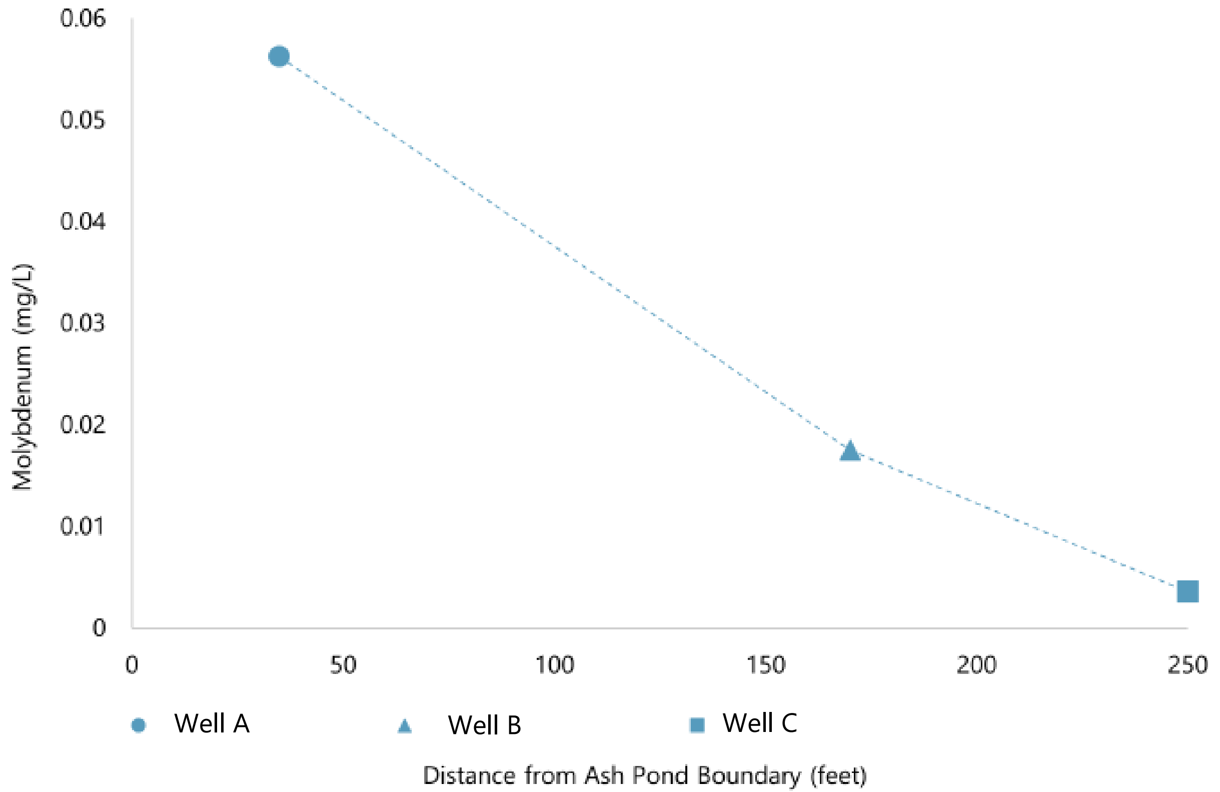


Decrease in magnitude and areal extent of arsenic through time

Decreasing Trends Through Time, Indicating Attenuation Regarding Groundwater Protection Standard (GWPS)



Example Concentration with Distance Along a Downgradient Flow Transect



Note:
mg/L: milligrams per liter

Attenuation Mechanisms Observed at Multiple CCR Sites

Attenuating Mechanism	Arsenic	Boron	Cobalt	Lithium	Molybdenum	Nickel	Zinc	Lead
Sorption on, and coprecipitation with, iron oxides and oxyhydroxides	X	X	X	X	X	X	X	X
Sorption on, and coprecipitation with, manganese oxides				X				
Ion exchange on clay minerals or other fine-grained materials (e.g., metal oxides)		X	X	X	X	X	X	
Precipitation of barium minerals	X							
Precipitation of calcium minerals					X			
Physical mechanisms (e.g., dispersion)	X	X	X	X	X	X	X	X

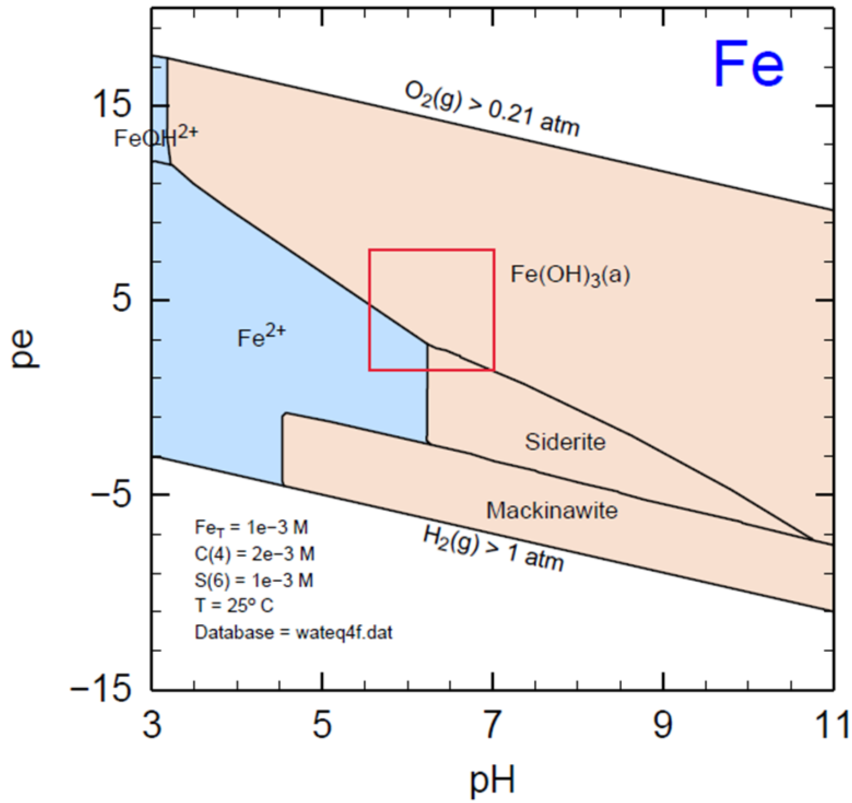
Protocol for Determining Mechanisms and Stability of Attenuation

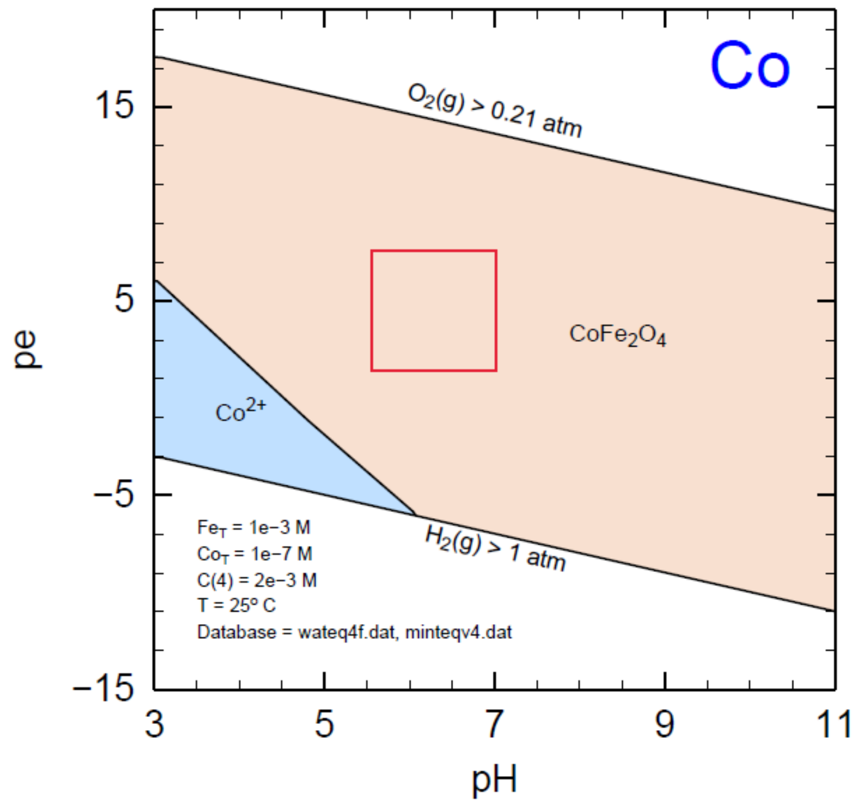
- Sample and analyze groundwater for major cations, anions, and constituents of interest; perform geochemical modeling using PHREEQC or similar software
- U.S. Environmental Protection Agency prefers tangible evidence
- Collect and analyze attenuating solids (precipitates and aquifer fines) from bottoms of wells
  - Bulk chemistry by X-ray fluorescence (XRF)
  - Mineralogy by X-ray diffraction (XRD)
  - Selective sequential extraction (SSE)
  - Cation exchange capacity (CEC)
  - Scanning electron microscopy (SEM) and associated chemical analysis
- Develop geochemical conceptual site model

Lines of Evidence for Attenuation Mechanisms

Mechanisms	Geochemical Modeling	XRF	XRD	SSE	CEC	SEM
Sorption on, and coprecipitation with, iron oxides and oxyhydroxides (arsenic, boron, cobalt, lithium, molybdenum, nickel, lead, and/or zinc)	X	X		X		X
Ion exchange on clays (boron, cobalt, lithium, molybdenum, nickel, and/or zinc)			X	X	X	X
Precipitation of barium or calcium minerals (arsenic and molybdenum)	X					

Example pe-pH Stability Diagrams for Dissolved and Solid Phases Indicating Attenuation

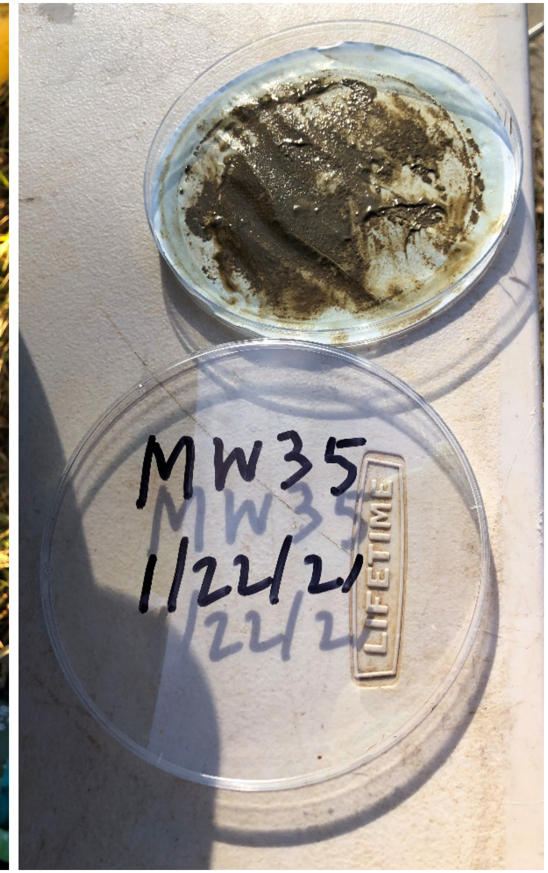




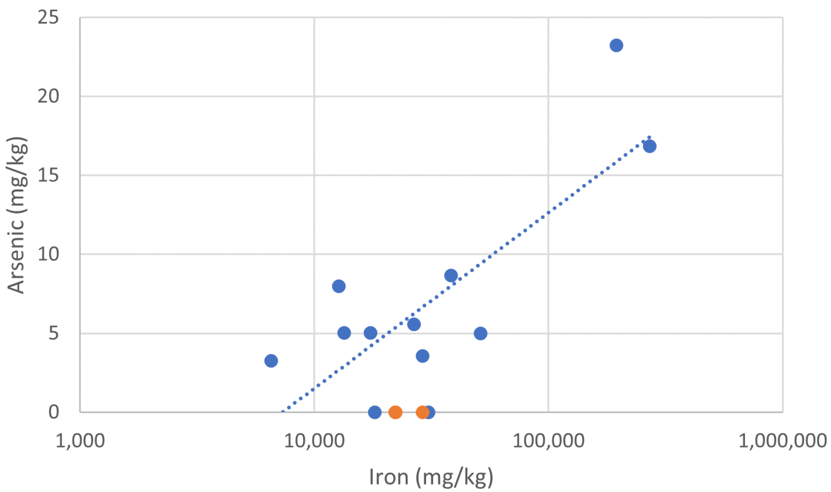
Notes:
Blue fields indicate dissolved/mobile species.
Tan fields indicate solid/attenuated species.
Red boxes indicate range of site pe-pH data.

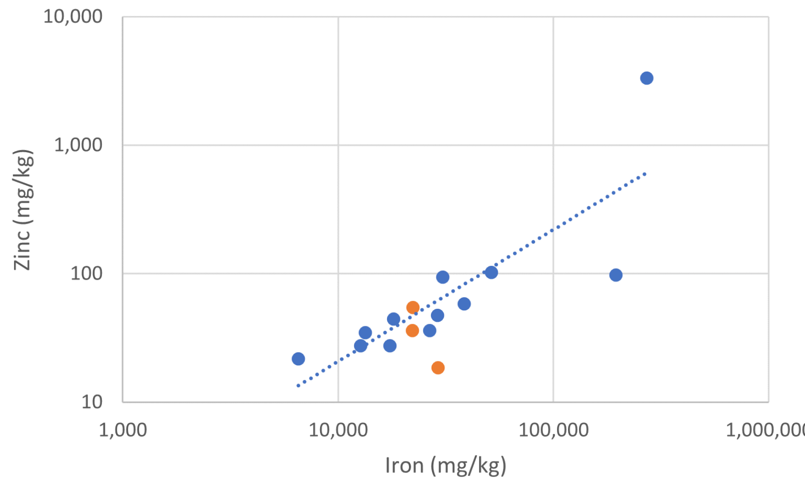
Observation of Iron Oxides in Site Aquifer Material

Solids Collection from Monitoring Wells

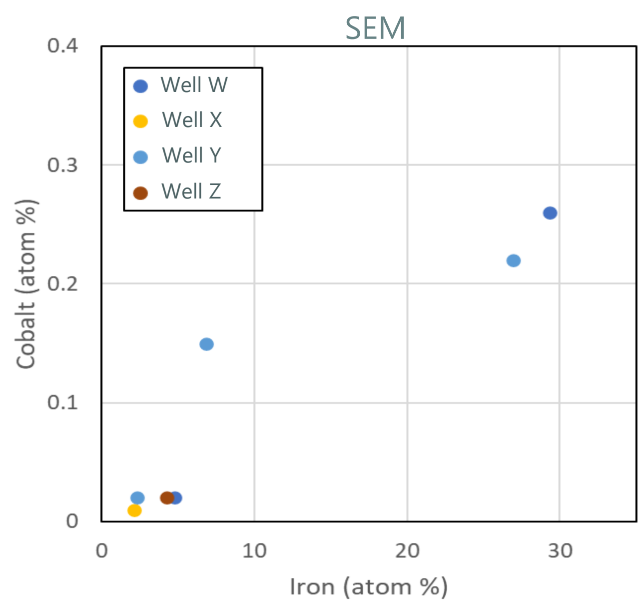


Bulk Chemistry Relationships Indicating Attenuation (from XRF and SEM)

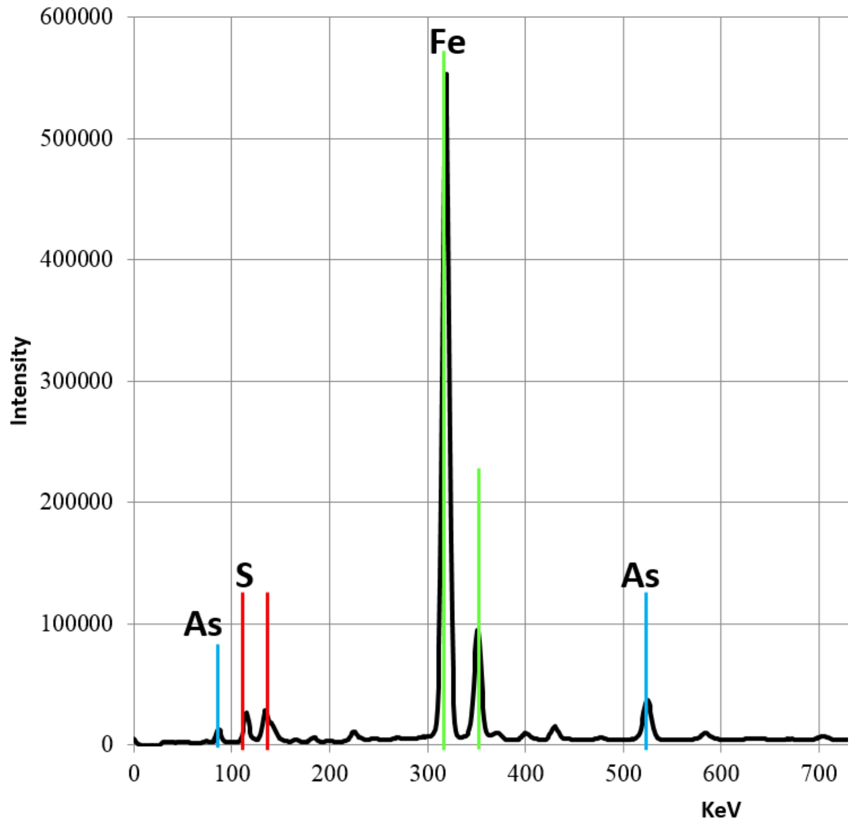




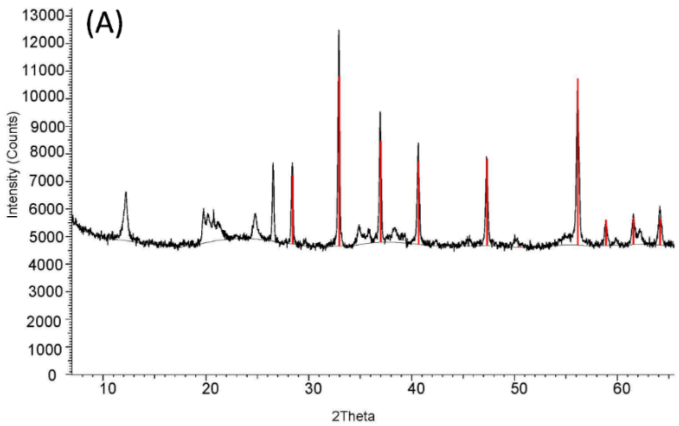
Notes for arsenic and zinc graphs:
Blue dots represent downgradient locations.
Orange dots represent upgradient locations.
mg/kg: milligrams per kilogram



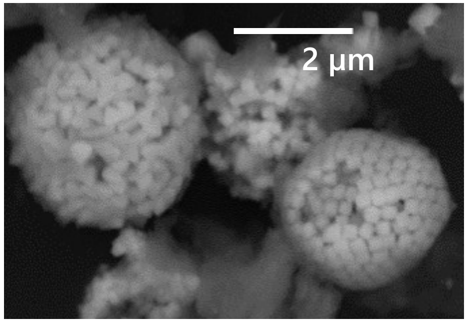
Evidence for Arsenic Attenuation in Sulfide Minerals



XRF spectra showing major components of pyrite (iron and sulfur) and attenuated arsenic



X-Ray diffractogram matching arsenic-substituted pyrite



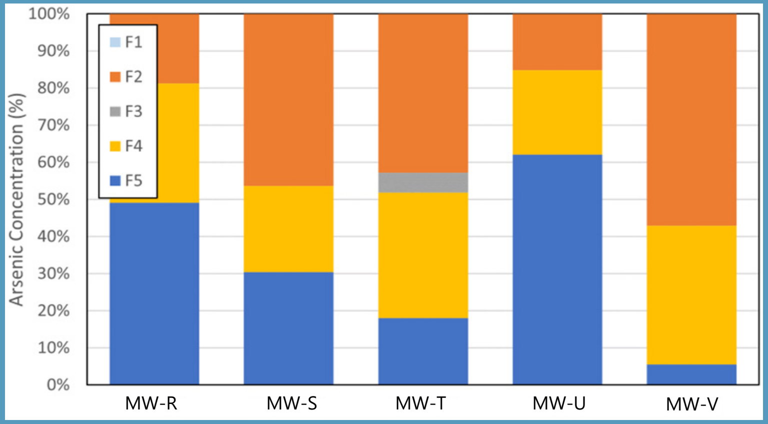
SEM image of framboidal pyrite in black precipitates

Minerals Identified by XRD, Weight %

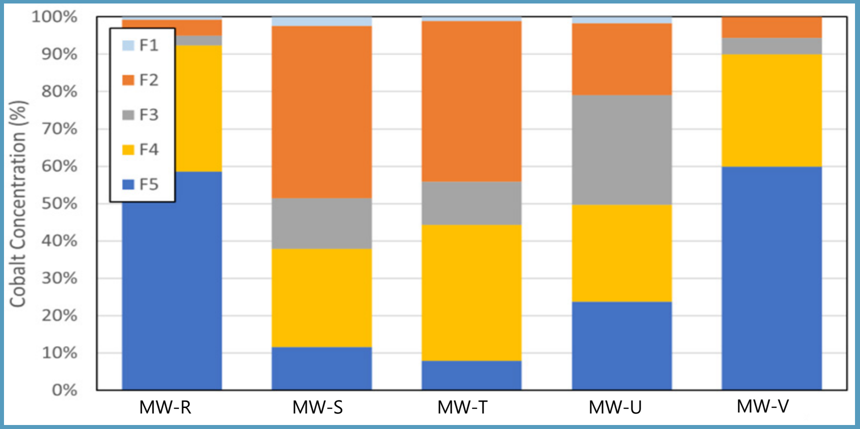
	Sample ID	Quartz	Feldspar	Mica		Clay Minerals					Carbonates	Cordierite
				Biotite	Muscovite/illite	Montmorillonite	Kaolinite	Vermiculite	Clinochlore	Greenalite	Calcite	
Well solids	Well R	51.8		--	39.6	--	--	--	8.6	--	--	--
Well solids	Well S	45.2	40.7	12.3	--	--	0.7	--	--	--	--	1.0
Well solids	Well T	43.5	33.6	19.0	--	--	--	--	--	1.0	--	3.0
Well solids	Well U	94.7	4.1	0.9	--	0.2	--	--	--	--	--	--
Well solids	Well V	27.8	38.1	25.6	--	--	--	--	--	--	8.6	--
Soil	Boring A	51.6	2.0	--	42.7	--	3.8	--	--	--	--	--
Soil	Boring B	35.6	9.7	--	41.6	--	13.1	0.1	--	--	--	--

Example SSE Results for Well Solids Samples

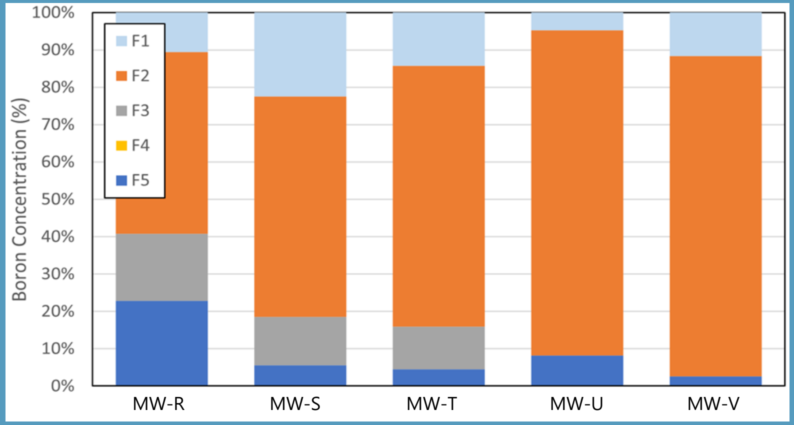
Arsenic



Cobalt



Boron

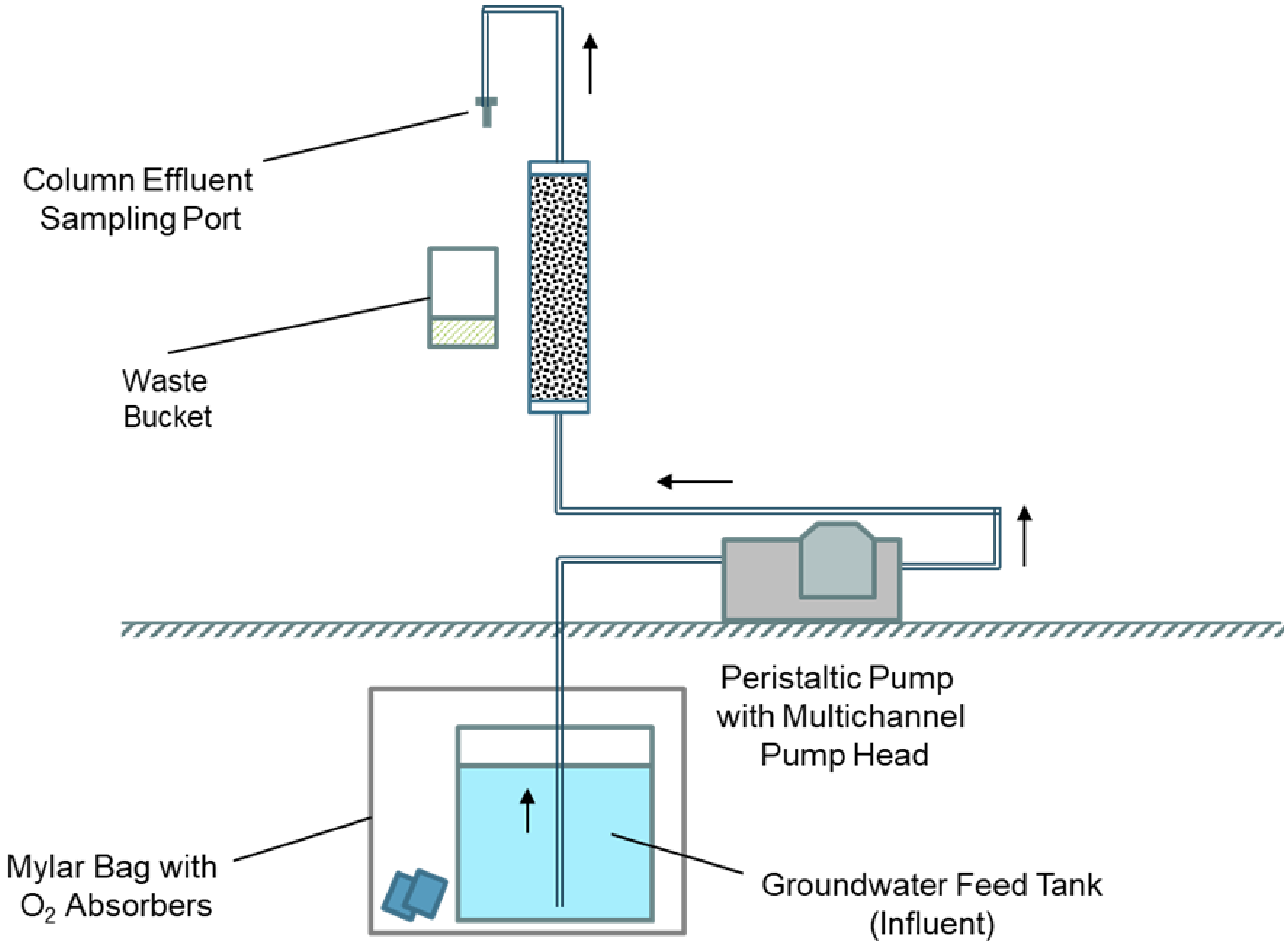


Fraction	Target Phases
F1	Water soluble
F2	Exchangeable (e.g., clay minerals)
F3	Reducible (e.g., amorphous metal oxides)
F4	Oxidizable (e.g., crystalline metal oxide and sulfide minerals)
F5	Residual (e.g., silicate minerals from aquifer matrix)

Cation Exchange Capacity of Well Solids, Milliequivalents per Kilogram

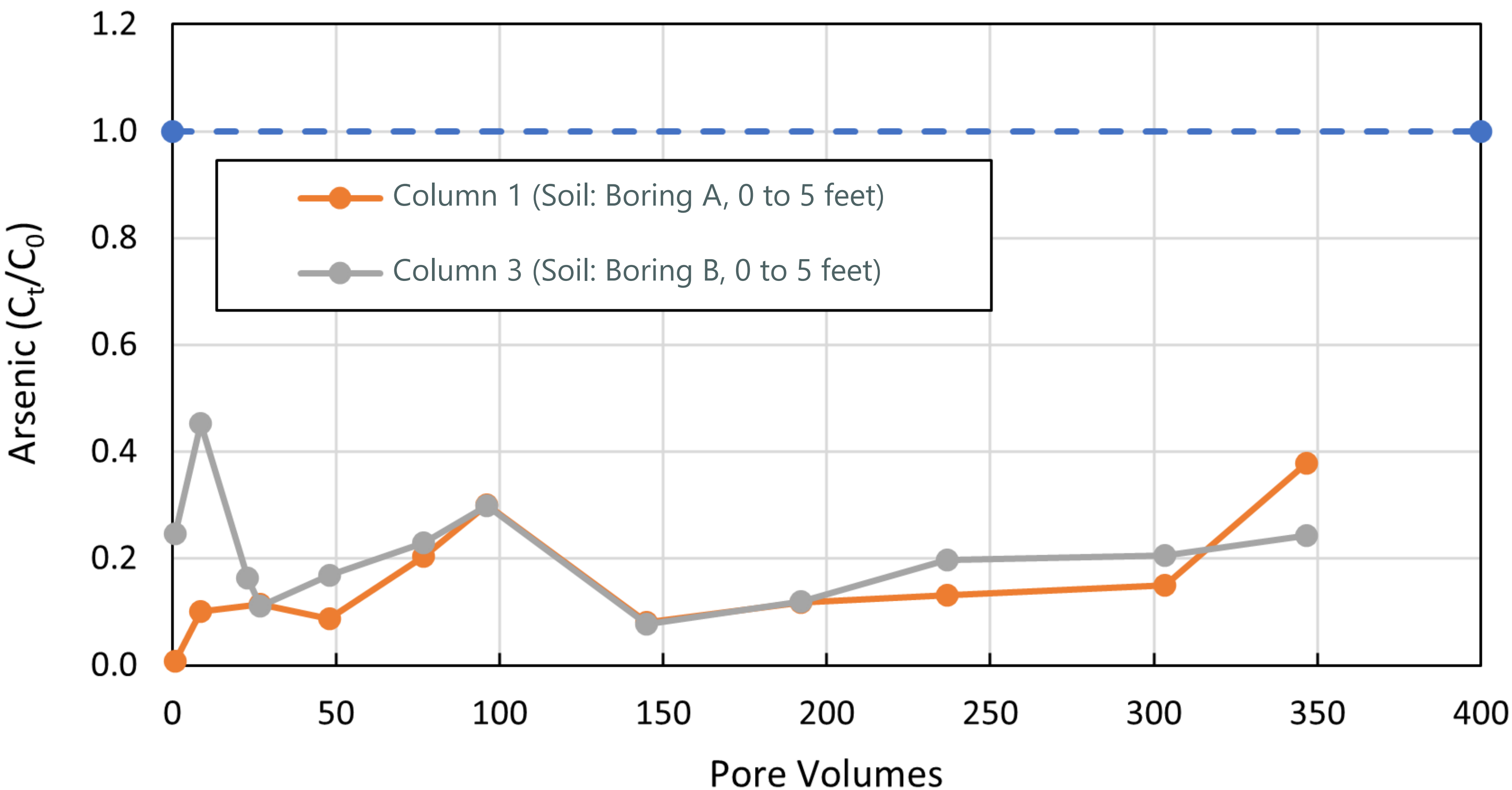
Well ID	Boron	Cobalt	Lithium	Molybdenum	Nickel
Well E	1.9	0.03	0.1	0.017	0.18
Well F	2.1	0.53	1.5	0.55	0.4
Well G	1.2	0.18	0.53	0.64	0.13
Well H	0.3	0.08	0.24	0.01	0.05
Well I	1	0.003	0.008	0.29	0.16
Well J	0.01	0.0006	0.002	0.0004	0.003
Well K	0.02	0.0009	0.003	0.001	0.006

Schematic of Column Test Setup



Column Test Equipment Setup

Example Breakthrough Curves from Columns



Notes:
Blue dashed line indicates effluent concentrations equal influent concentrations (i.e., capacity for attenuation has been consumed).
C_t/C_0: concentration ratio of effluent to influent

Site-Specific Conclusions (Three Sites)

- Multiple attenuating mechanisms identified
- Generally high capacity of surficial aquifers for attenuation
- Relatively high stability of the host minerals and attenuated constituents of interest (COIs)
- Times to achieve groundwater protection standards ranged from 3 to 55 years
  - 30 years or less, within closure period, for most
  - Reasonable compared to more aggressive groundwater corrective action technologies such as pump-and-treat or permeable reactive barrier walls

Questions/Discussion