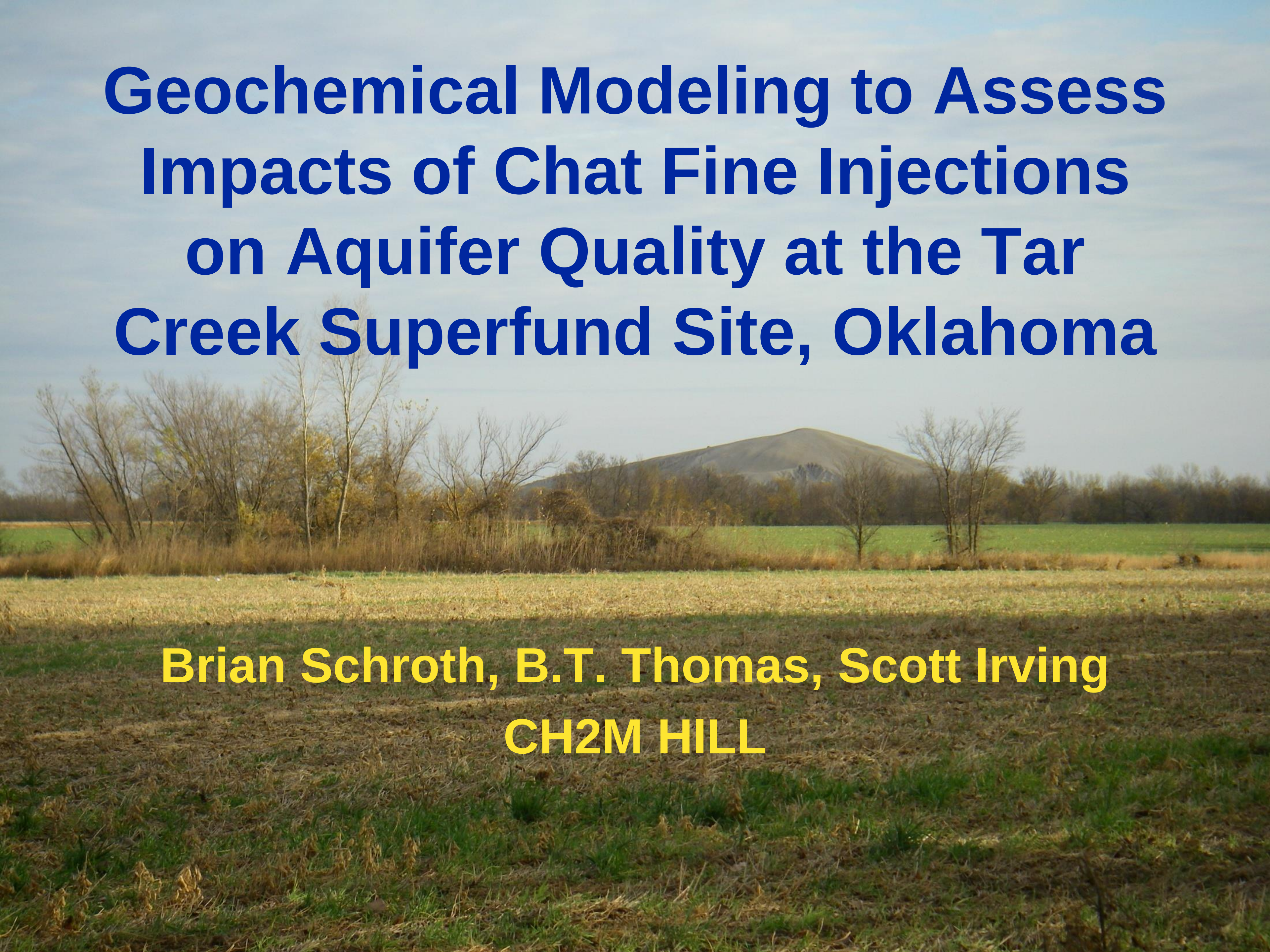
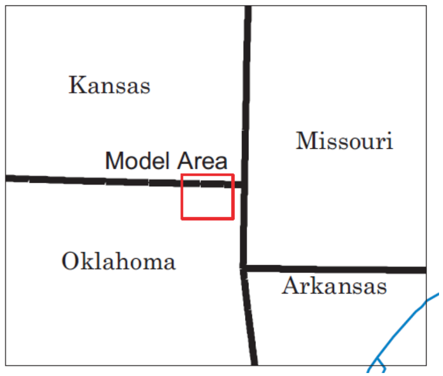
Geochemical Modeling to Assess Impacts of Chat Fine Injections on Aquifer Quality at the Tar Creek Superfund Site, Oklahoma

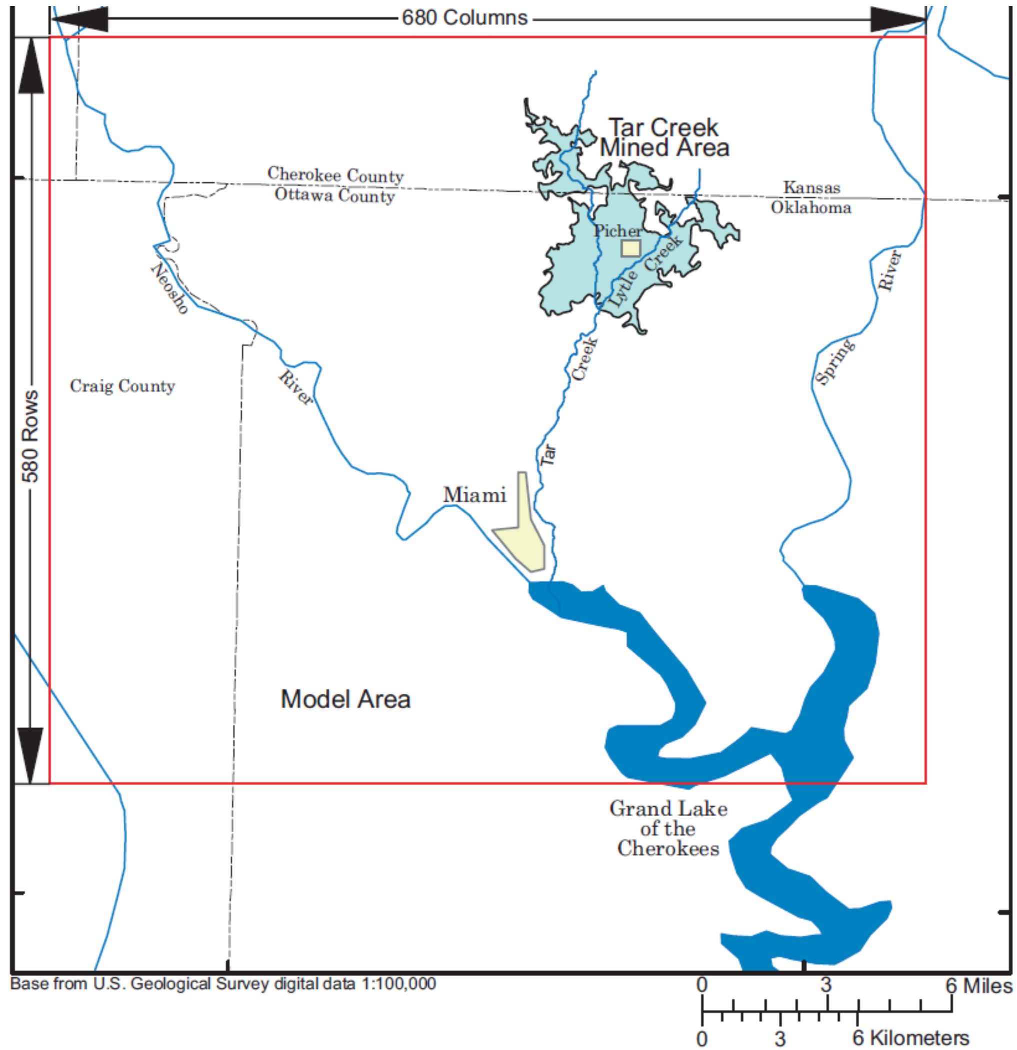


Brian Schroth, B.T. Thomas, Scott Irving

CH2M HILL

Study Region





Legacy of Tri-State Lead-Zinc Mining

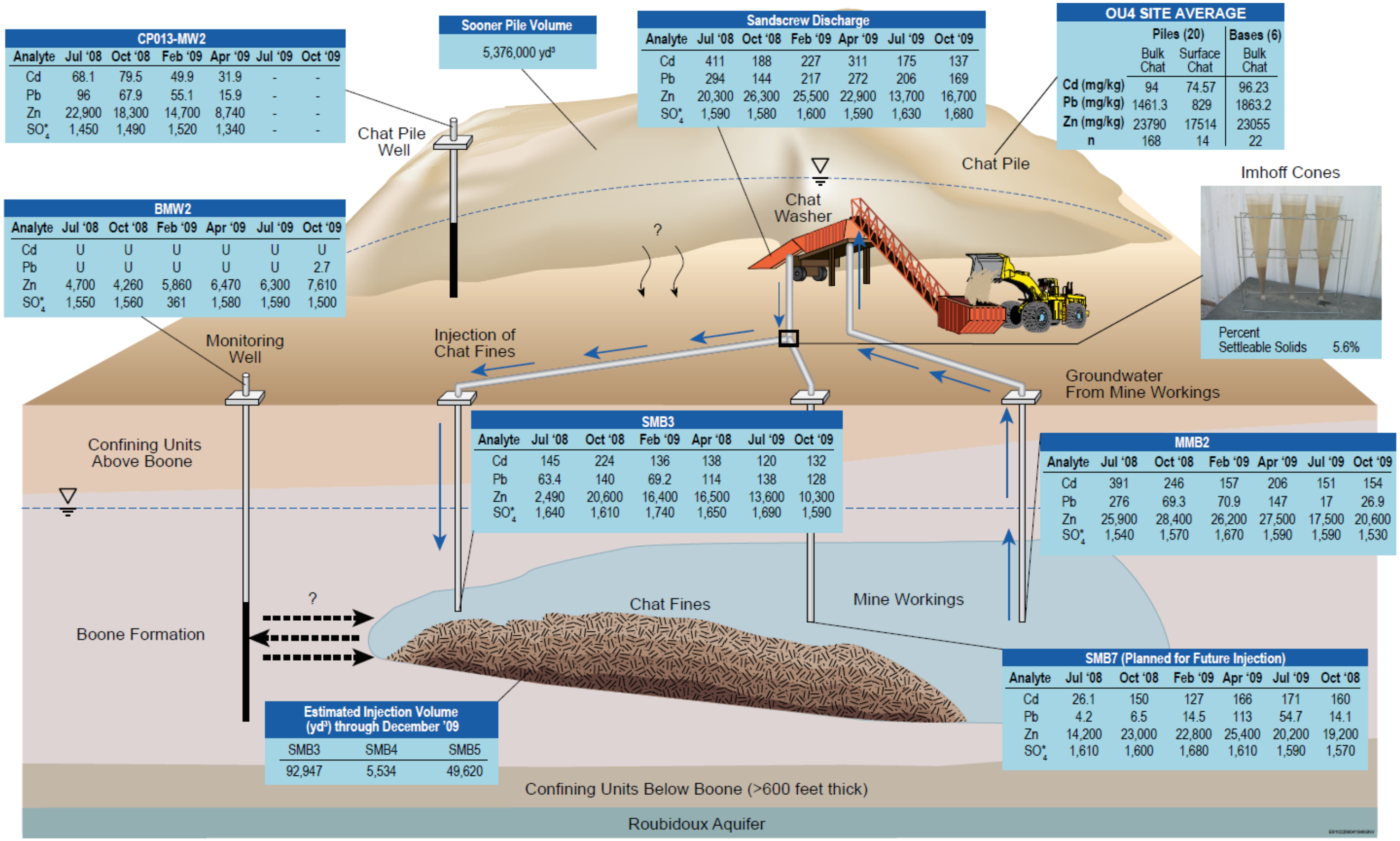
Study Objectives

- **Reduce dust hazard by removing chat piles**
- **Separate coarse chat (usable for road base) from fine chat**
- **Inject fine chat slurry into mine rooms below piles**
- **Conduct long-term pilot study to assess feasibility and monitor water quality**
- **Sooner Pile chosen as test area**
- **Use geochemical modeling to**
  - Verify observed results
  - Predict long term effects on water quality

From Top of Sooner Pile

Sooner Injection Pilot Study

CSM for Sooner Pile Chat Washing & Fines Injection



CP013-MW2

Analyte	Jul '08	Oct '08	Feb '09	Apr '09	Jul '09	Oct '09
Cd	68.1	79.5	49.9	31.9	-	-
Pb	96	67.9	55.1	15.9	-	-
Zn	22,900	18,300	14,700	8,740	-	-
SO_4^*	1,450	1,490	1,520	1,340	-	-

Sooner Pile Volume

5,376,000 yd^3

Sandscrew Discharge

Analyte	Jul '08	Oct '08	Feb '09	Apr '09	Jul '09	Oct '09
Cd	411	188	227	311	175	137
Pb	294	144	217	272	206	169
Zn	20,300	26,300	25,500	22,900	13,700	16,700
SO_4^*	1,590	1,580	1,600	1,590	1,630	1,680

OU4 SITE AVERAGE

	Piles (20)		Bases (6)
	Bulk Chat	Surface Chat	Bulk Chat
Cd (mg/kg)	94	74.57	96.23
Pb (mg/kg)	1461.3	829	1863.2
Zn (mg/kg)	23790	17514	23055
n	168	14	22

BMW2

Analyte	Jul '08	Oct '08	Feb '09	Apr '09	Jul '09	Oct '09
Cd	U	U	U	U	U	U
Pb	U	U	U	U	U	2.7
Zn	4,700	4,260	5,860	6,470	6,300	7,610
SO_4^*	1,550	1,560	361	1,580	1,590	1,500

SMB3

Analyte	Jul '08	Oct '08	Feb '09	Apr '08	Jul '09	Oct '09
Cd	145	224	136	138	120	132
Pb	63.4	140	69.2	114	138	128
Zn	2,490	20,600	16,400	16,500	13,600	10,300
SO_4^*	1,640	1,610	1,740	1,650	1,690	1,590

MMB2

Analyte	Jul '08	Oct '08	Feb '09	Apr '09	Jul '09	Oct '09
Cd	391	246	157	206	151	154
Pb	276	69.3	70.9	147	17	26.9
Zn	25,900	28,400	26,200	27,500	17,500	20,600
SO_4^*	1,540	1,570	1,670	1,590	1,590	1,530

Estimated Injection Volume (yd^3) through December '09

SMB3	SMB4	SMB5
92,947	5,534	49,620

SMB7 (Planned for Future Injection)

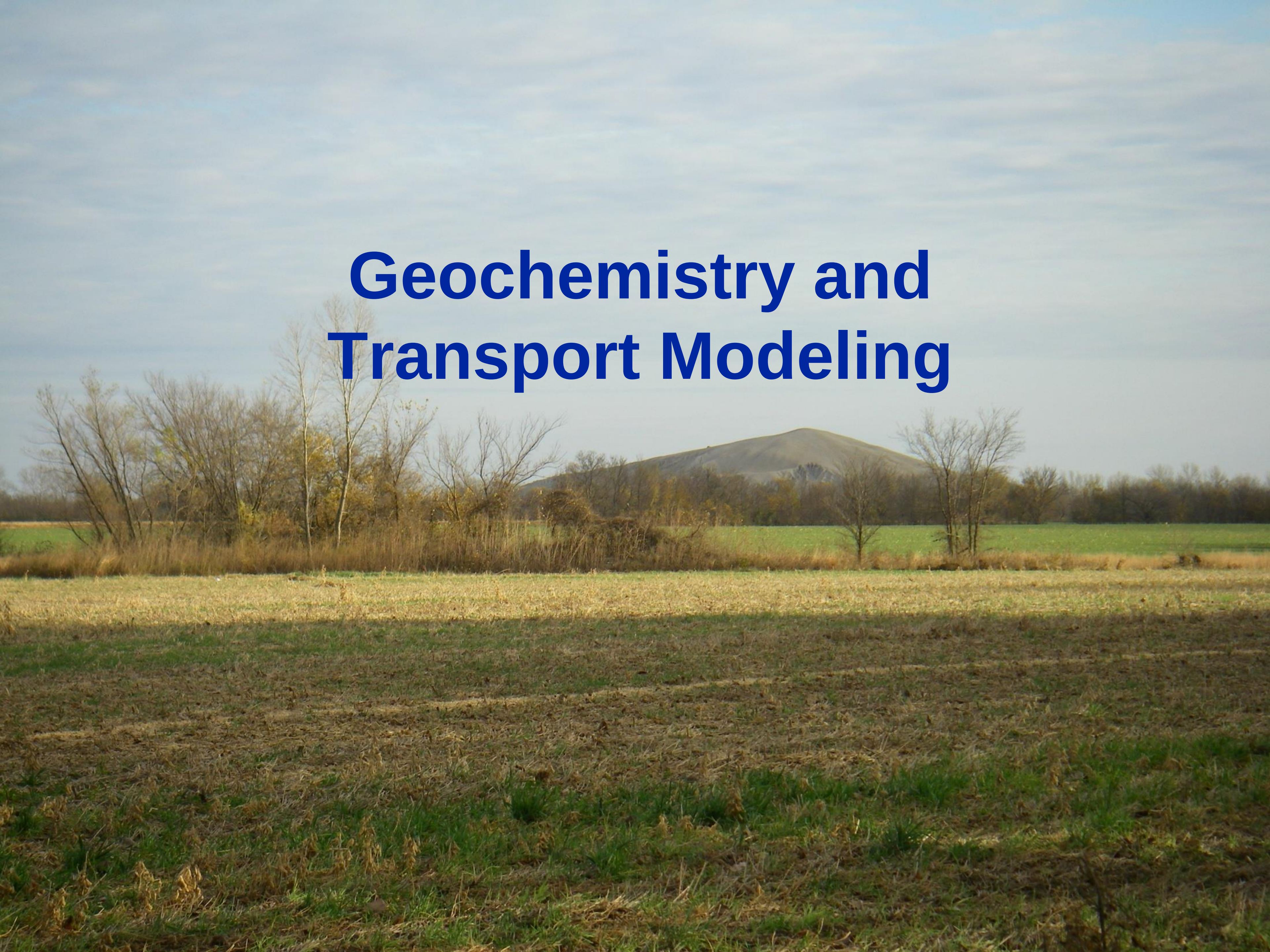
Analyte	Jul '08	Oct '08	Feb '09	Apr '09	Jul '09	Oct '08
Cd	26.1	150	127	166	171	160
Pb	4.2	6.5	14.5	113	54.7	14.1
Zn	14,200	23,000	22,800	25,400	20,200	19,200
SO_4^*	1,610	1,600	1,680	1,610	1,590	1,570

Note: Unless otherwise noted, the analytical results are reported in µg/L
U = Non-detect
* = Results reported in mg/L

Chat Size Fraction Separator ("Sandscrew")

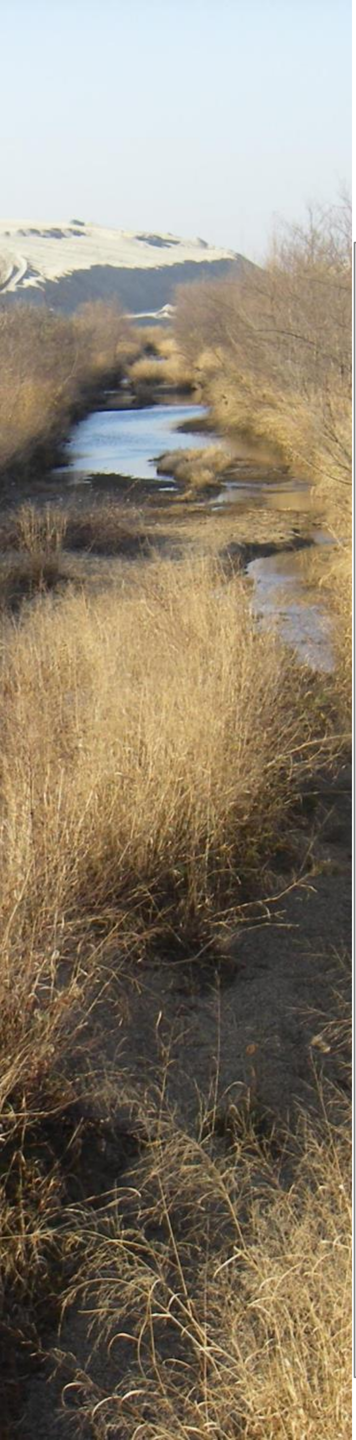
Chat Size Fraction Separator (“Sandscrew”)

Injection of Fines Slurry

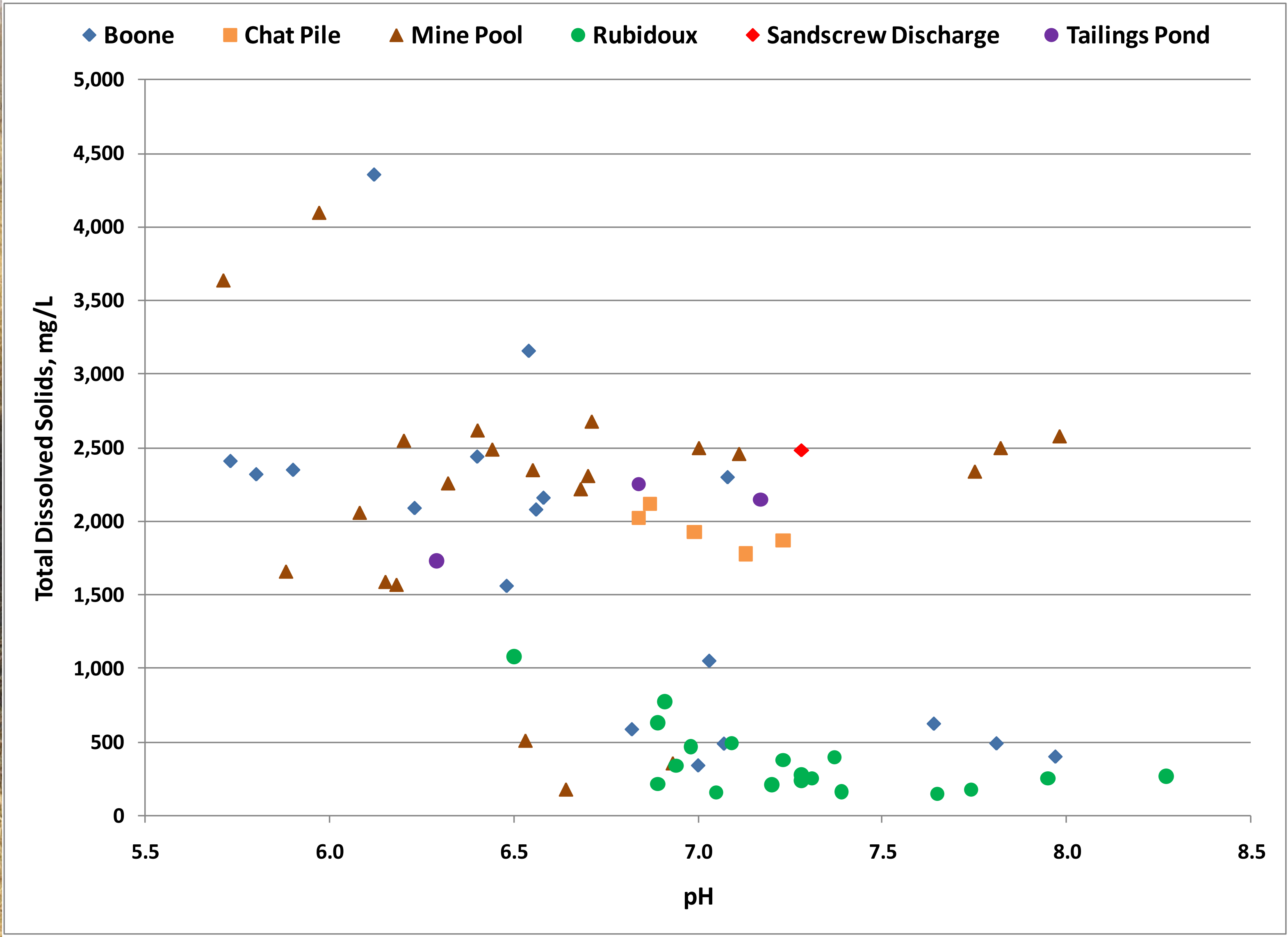

Geochemistry and
Transport Modeling

Geochemical Signatures

- **Boone Aquifer**
  - Mineralized zones: Ca-SO_4, high TDS, trace metals
  - Non-mineralized: variable chem, low TDS, low trace metals
- **Mine Pool Water**
  - Ca-SO4, Higher TDS than Boone, trace metals
- **Rubidoux**
  - Ca/Mg-HCO_3/SO_4, low TDS, very low trace metals

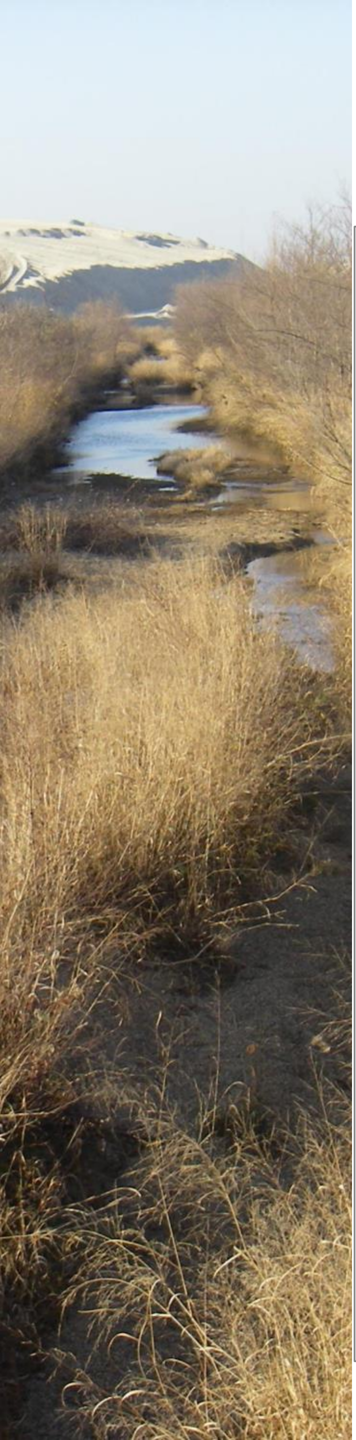


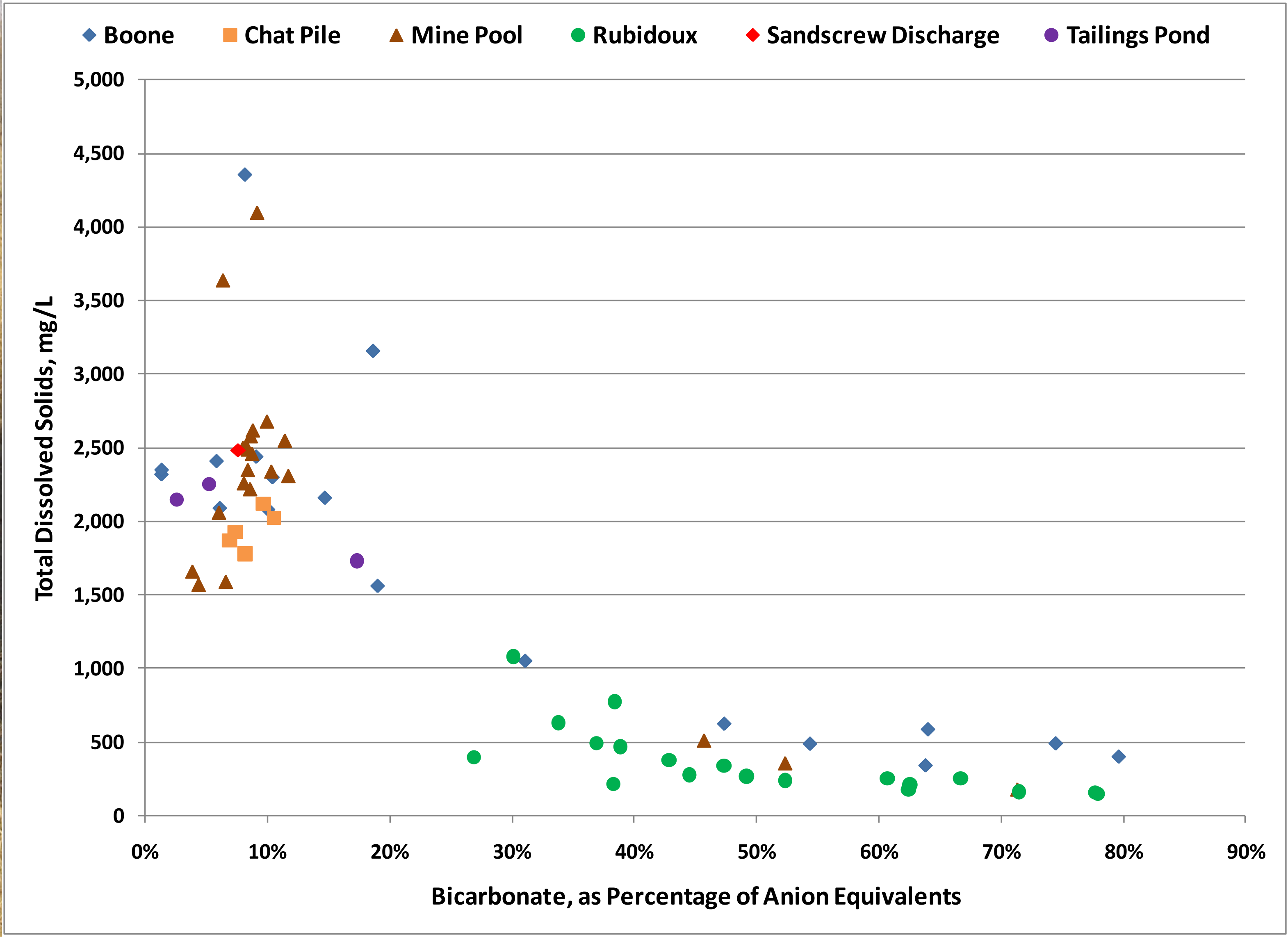
TDS vs. pH

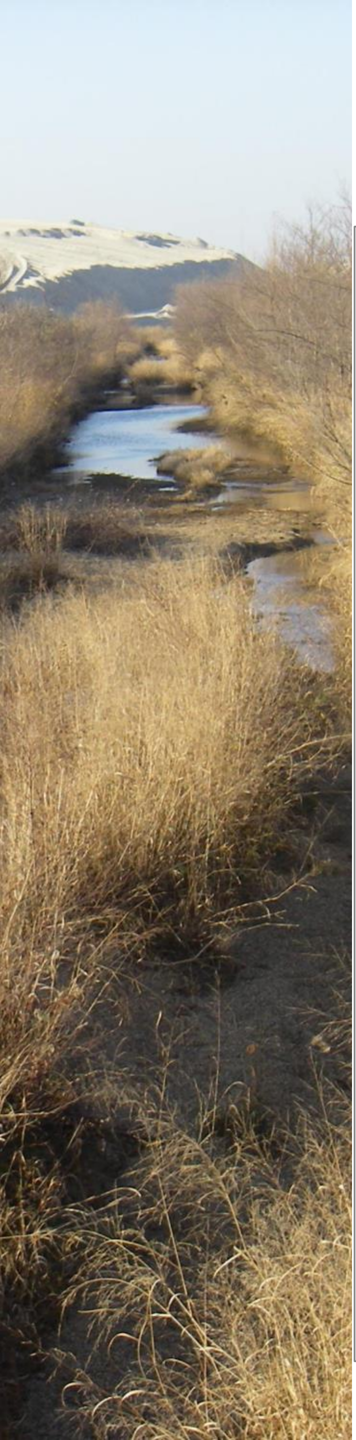


Boone
Chat Pile
Mine Pool
Rubidoux
Sandscrew Discharge
Tailings Pond
Total Dissolved Solids, mg/L
5,000
4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
pH

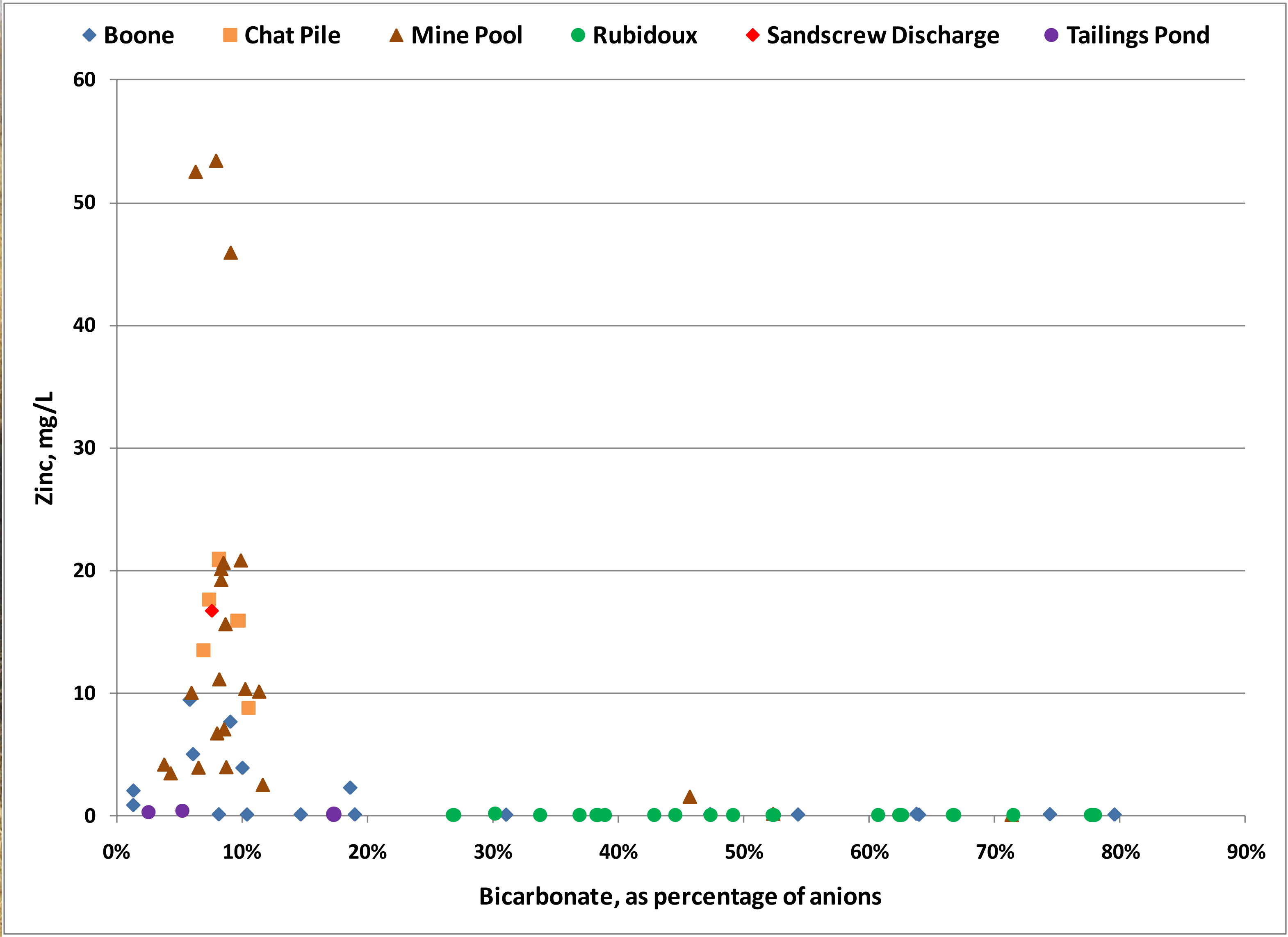
TDS vs. Bicarbonate Pct.



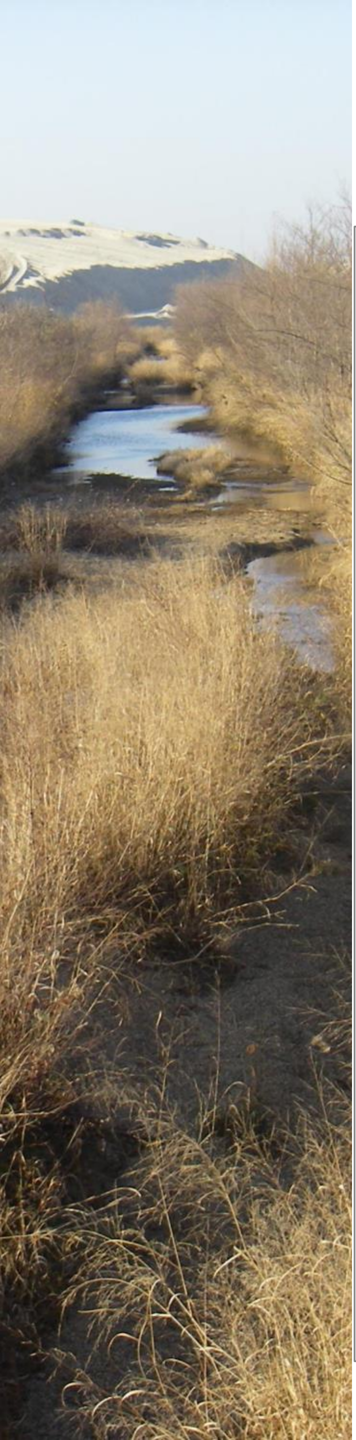


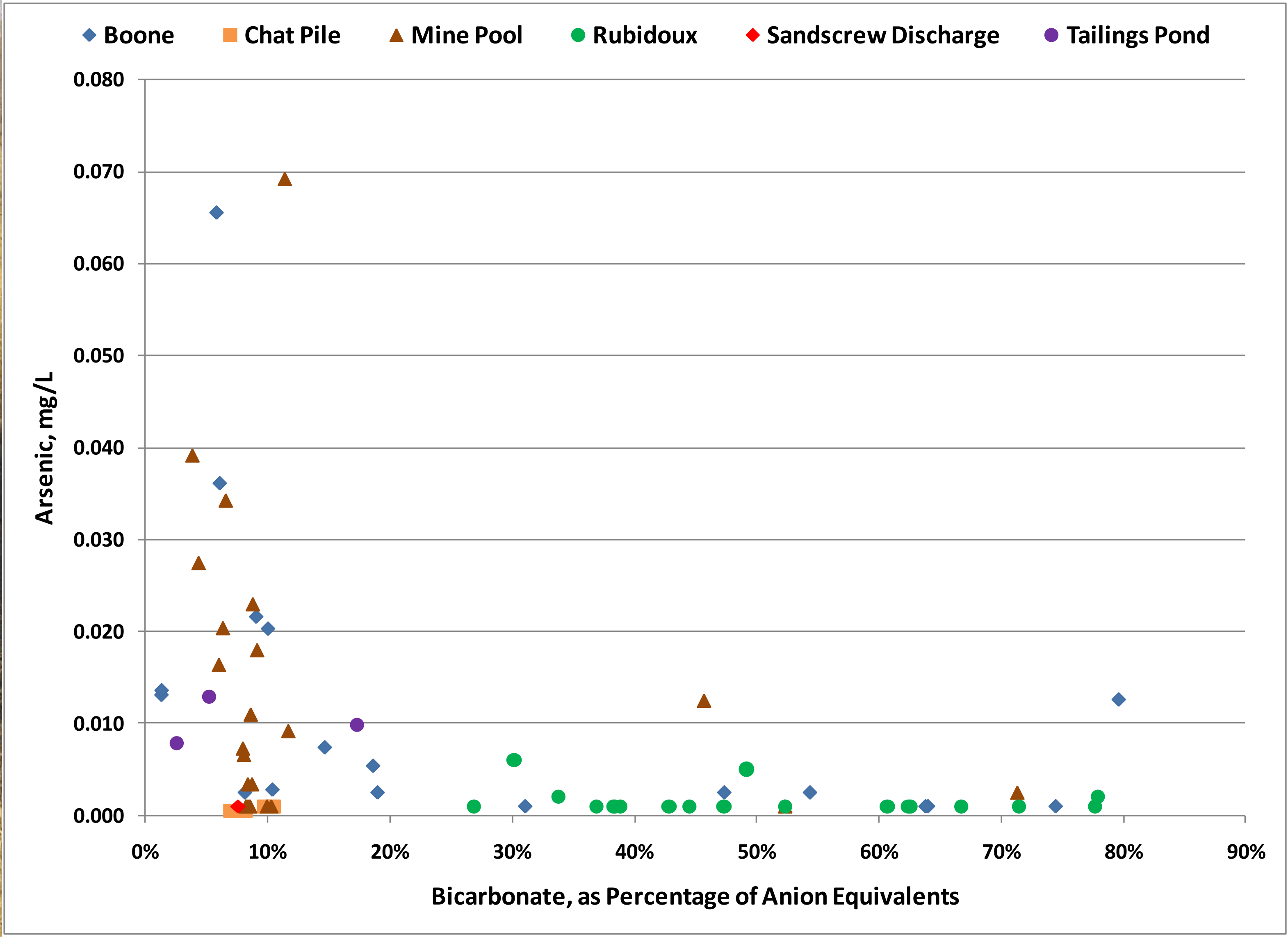


Zinc vs. Bicarbonate Pct.



Arsenic vs. Bicarbonate Pct.





Chat and Chat Fines Composition – XRD Analysis

- Bulk chat primarily comprised of chert (amorphous SiO_2) – over 90%
- Minor carbonates (calcite, dolomite)
- Trace sulfide, oxide, clay minerals
- Fine fractions shown to have higher concentrations of metals

Chat and Chat Fines Modeled Trace Metal Minerals

- **Primary Minerals**
  - Sphalerite (ZnS); Cd associated
  - Galena (PbS)
  - Pyrite (FeS_2); As associated
- **Secondary Minerals**
  - Carbonates of Zn, Cd, Pb, and Fe
  - Sulfates of Pb, Fe
  - Minor silcates (hemimorphite = Zn source)
  - Oxides of Cd, Fe (plus adsorbed metals on FeO's)

Reactions During Injection

- **Chat fines mixed with mine pool water**
  - Dissolves minerals in fines, releasing trace metals
  - Carbonates buffer acidity released by sulfide oxidation
  - Mixing at surface ensures oxygen presence in solution
  - Process modeled with PHREEQC

Reactions During Injection
(cont'd)

- **Chat fines slurry injected into mine pool**
  - Oxygen-rich water mixes locally with more reduced mine pool water and iron oxides precipitate
  - Iron oxides act as co-precipitates with and adsorbents for trace metals (especially arsenic and lead)
  - Process modeled with PHREEQC

PHREEQC Model

- **Observed minerals in chat are added to Sooner Pilot Study supply water (MMB2)**
  - Zinc, lead, and cadmium sulfides
  - Calcite and dolomite
  - Resulting water reasonably resembles slurry water injected into mine pool
- **Slurry water is mixed with mine pool water in various proportions with mineral precipitation and dissolution controls**
  - Solubility controlled by sulfate and carbonate minerals
  - Result resembles injection well samples if ratio of mine pool water to slurry water is 2:1

PHREEQC Model Results

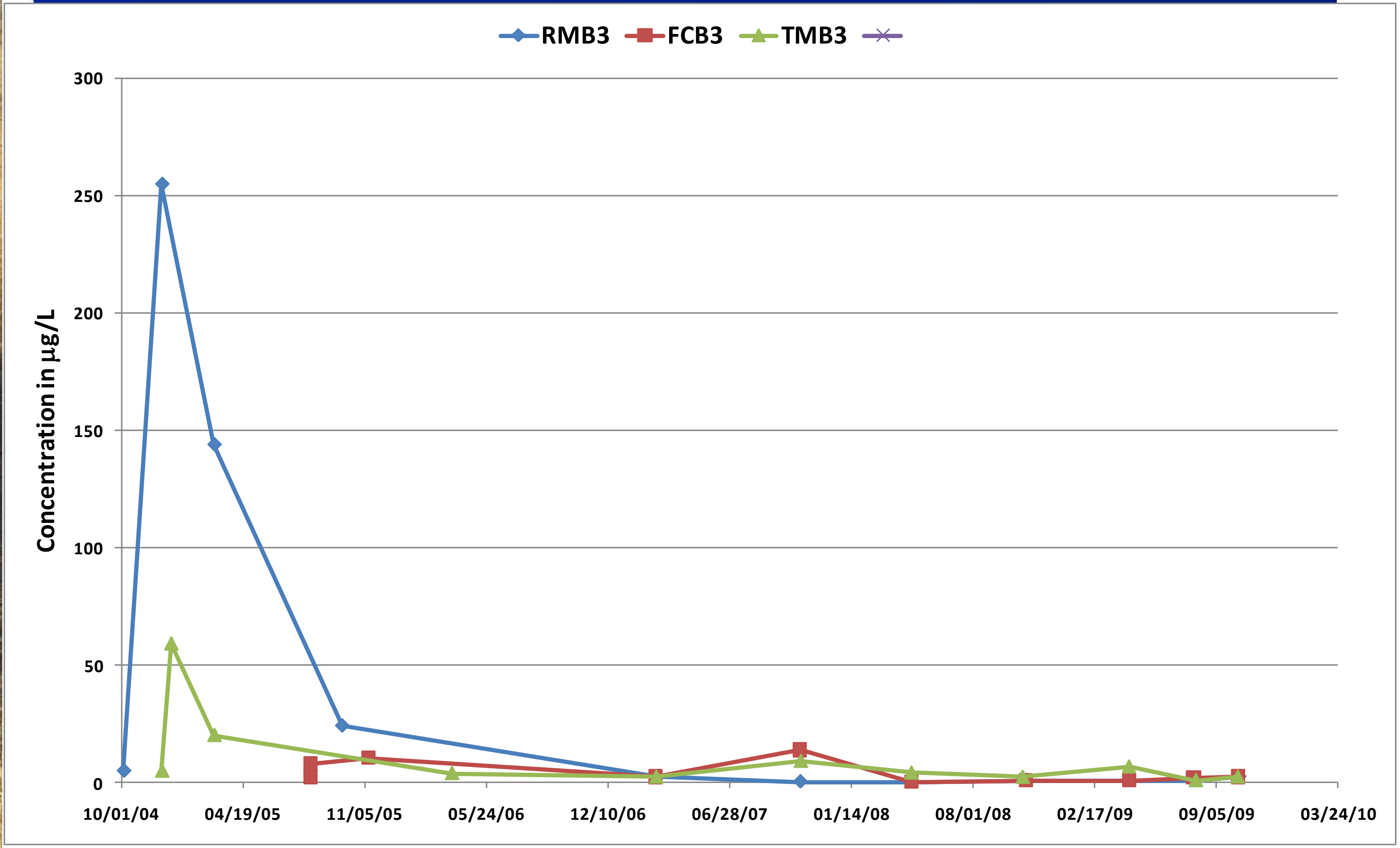
Dissolution of cadmium, lead, and zinc sulfides and calcium/magnesium carbonate; Precipitation of calcium, zinc, and cadmium carbonates and of iron oxide

			Metals in ug/L			
Description	**Sample ID**	**Date**	**Fe**	**Zn**	**Cd**	**Pb**
Mine pool water used to slurry fine chat	MMB2	07/17/08	391	25,900	391	276
Water portion of fine chat slurry in sandscrew tank	SNDSCR	07/17/08	<25	20,300	411	294
	PHREEQC simulation results		<25	20,967	339	318

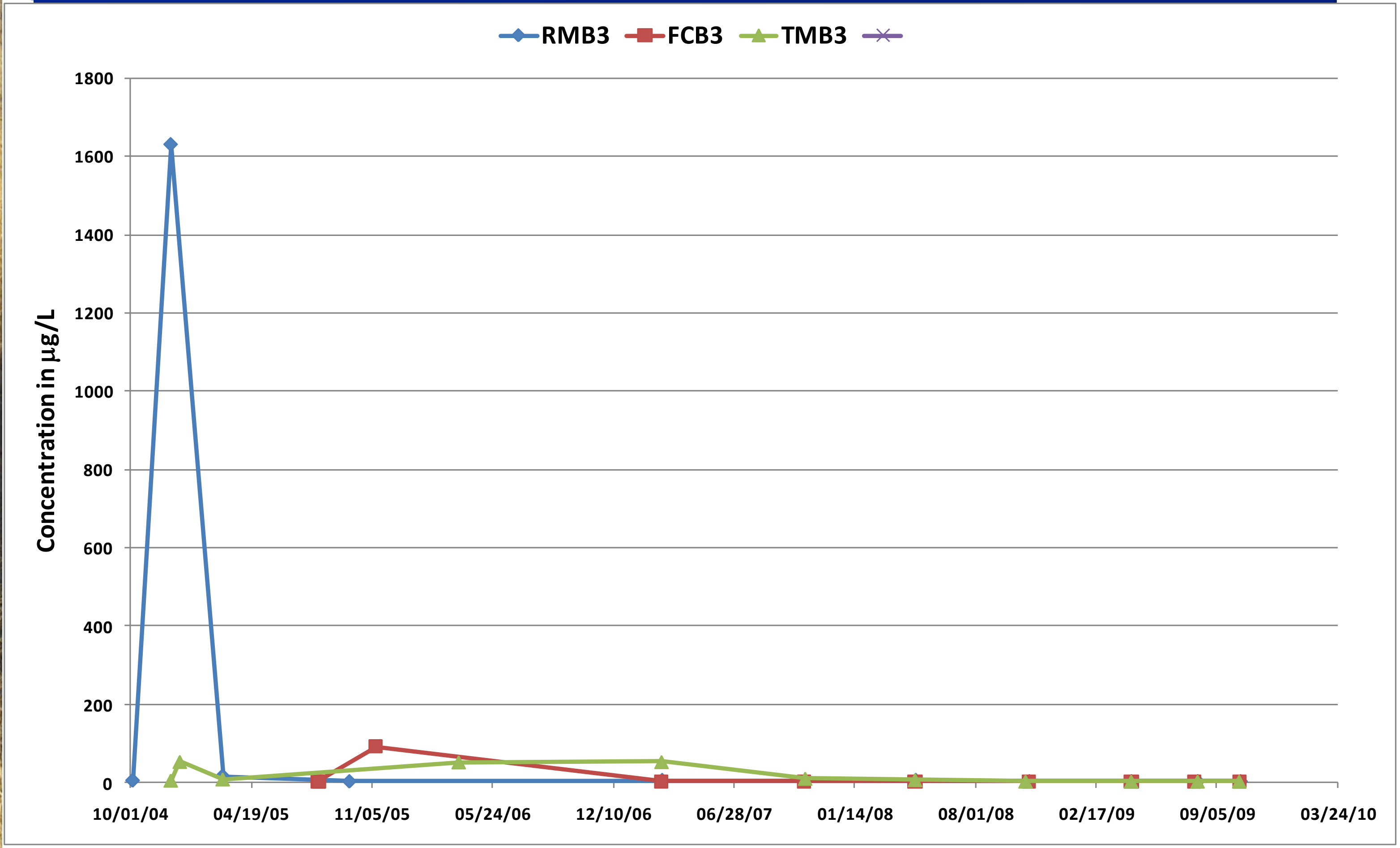
Mix pre-injection mine pool water with SNDSCR water in the ratio 2:1; Dissolution of gypsum; Precipitation of iron oxide

			Metals in ug/L			
Description	**Sample ID**	**Date**	**Fe**	**Zn**	**Cd**	**Pb**
Pre-injection mine pool water at Sooner Pile	SMB2	07/11/07	11,900	11,800	8.3	3.3
Water portion of fine chat slurry in sandscrew tank	SNDSCR	07/17/08	<25	20,300	411	294
First post-injection mine pool sample at Sooner Pile	SMB2	10/24/07	<25	20,100	246	78.1
	PHREEQC simulation results		<25	14,666	143	100

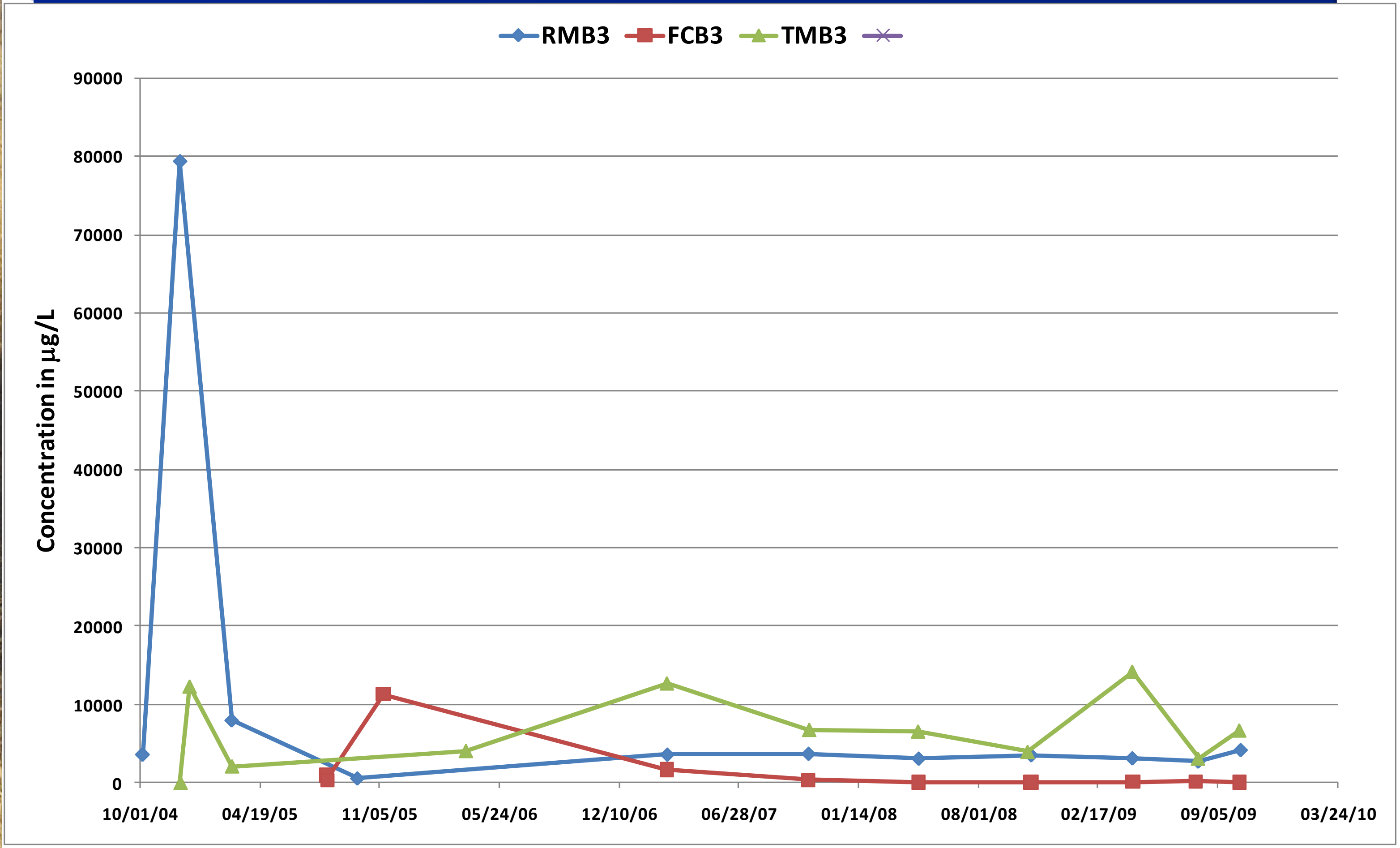
Short-Term Pilot Studies: Lead



Short-Term Pilot Studies: Cadmium



Short-Term Pilot Studies: Zinc



PHAST Model

- **Groundwater flow and solute transport model combined with PHREEQC**
- **Transport simulated with parameters from site groundwater flow model (conductivity, gradients) and modified with transport parameters**
  - Dispersion
  - Cation exchange
  - Adsorption
  - Mineral precipitation

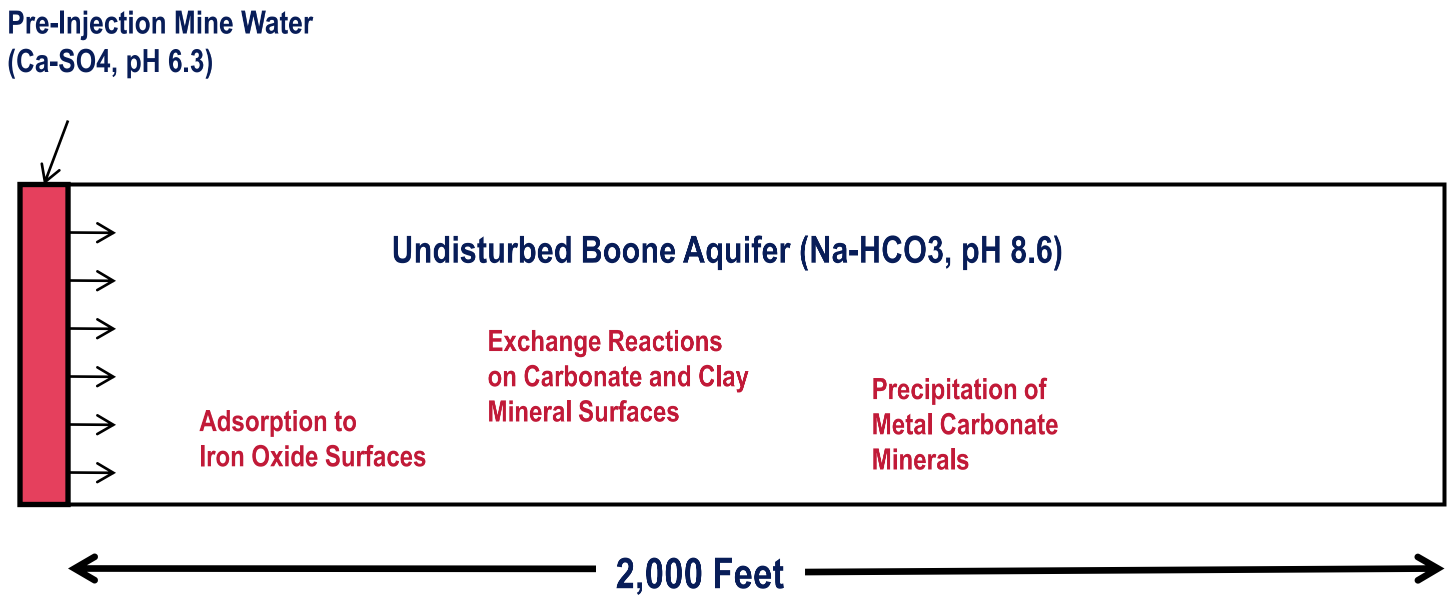
PHAST Simulations

- Pre-injection mine water introduced as continuous flow into Boone Aquifer (outside of mine influence): 40 years
- Sooner injection well data were diluted based on results from dilution simulation within mine workings: 5-year injection
- Diluted water flows into Boone: 20 years
- One-dimensional flow was simulated for simplicity

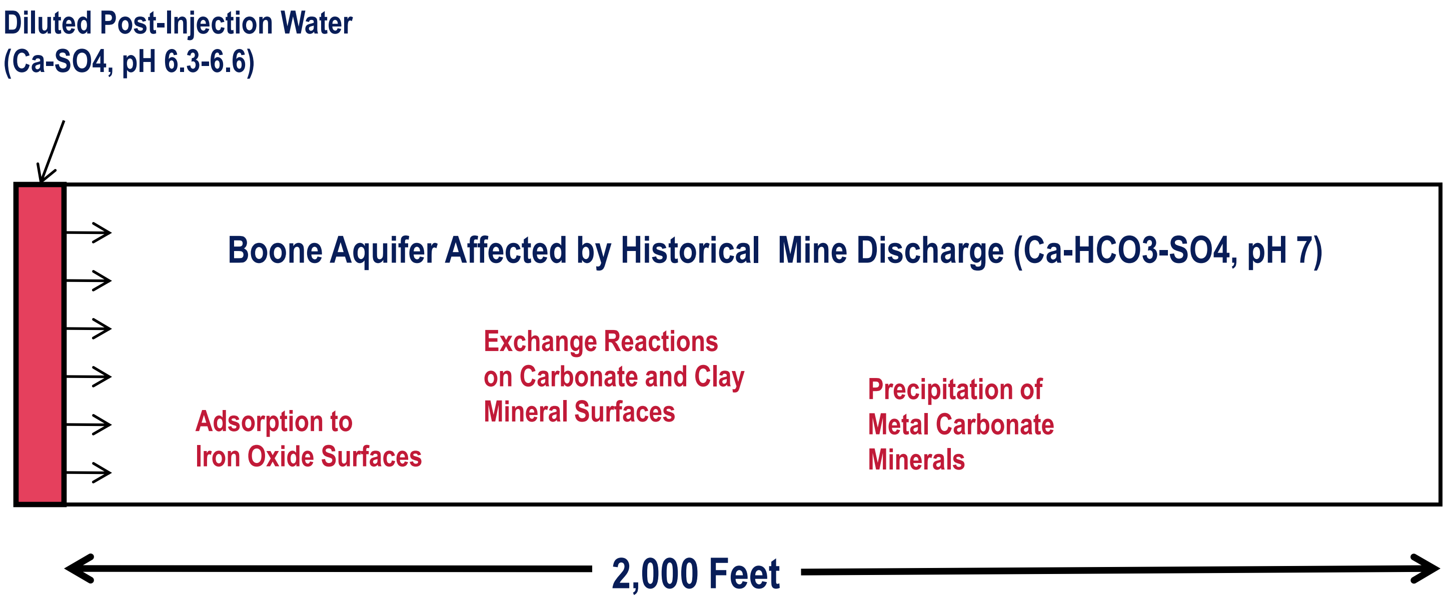
PHAST Simulations

- Post-injection water represented by October 2009 sample from well SMB3 – washed fines injection well from Sooner Pile
- General mine pool water represented by pre-injection sample from well SMB2 – also from Sooner Pile
- These two waters were mixed in different proportions using PHREEQC to represent different stages of discharge into Boone
- Boone aquifer represented by well BW13 – outside of mine influence

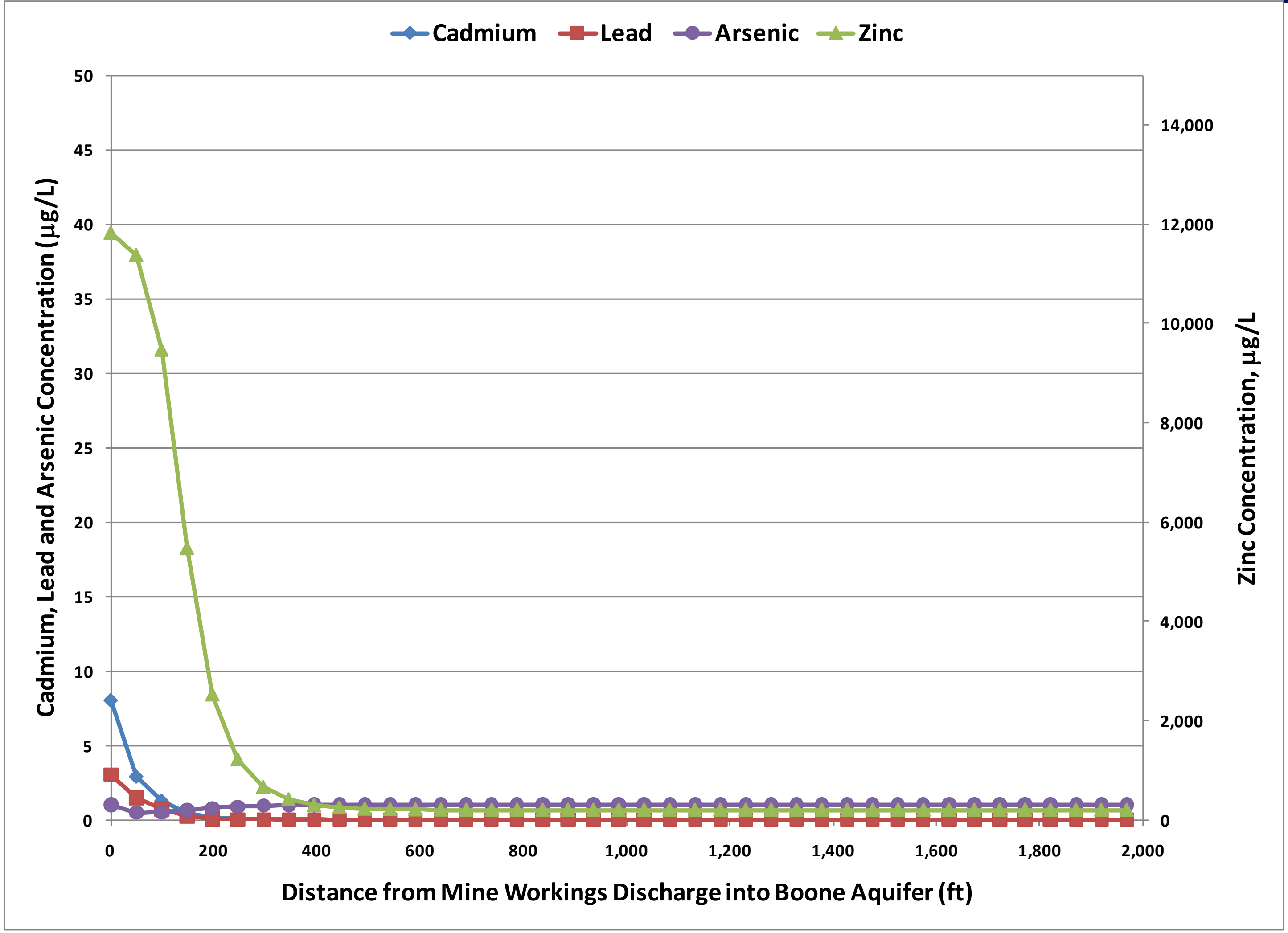
PHAST Model Layout: Phase 1



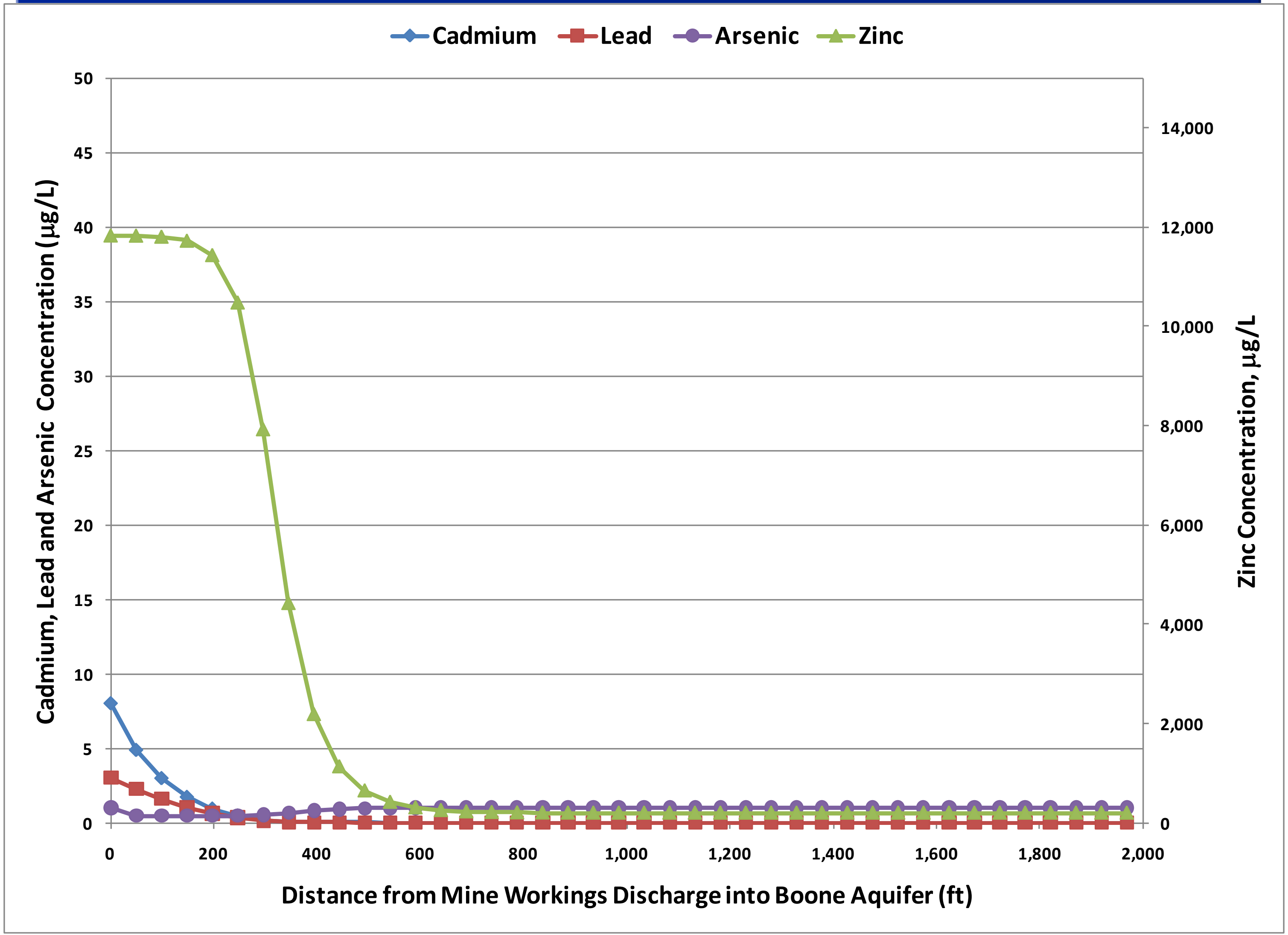
PHAST Model Layout: Phase 2



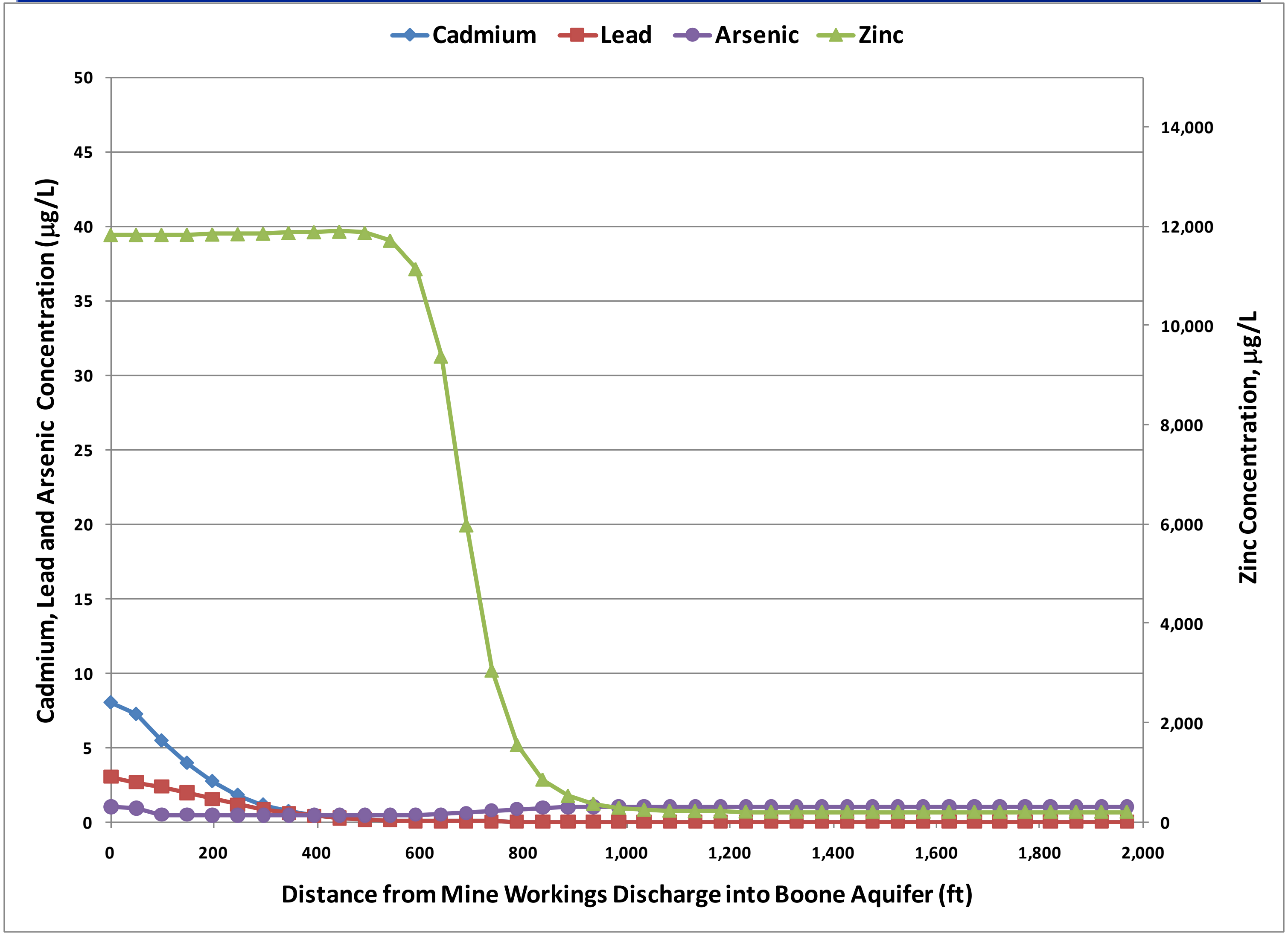
PHAST Model Results
Phase 1: 10 years (~1980)



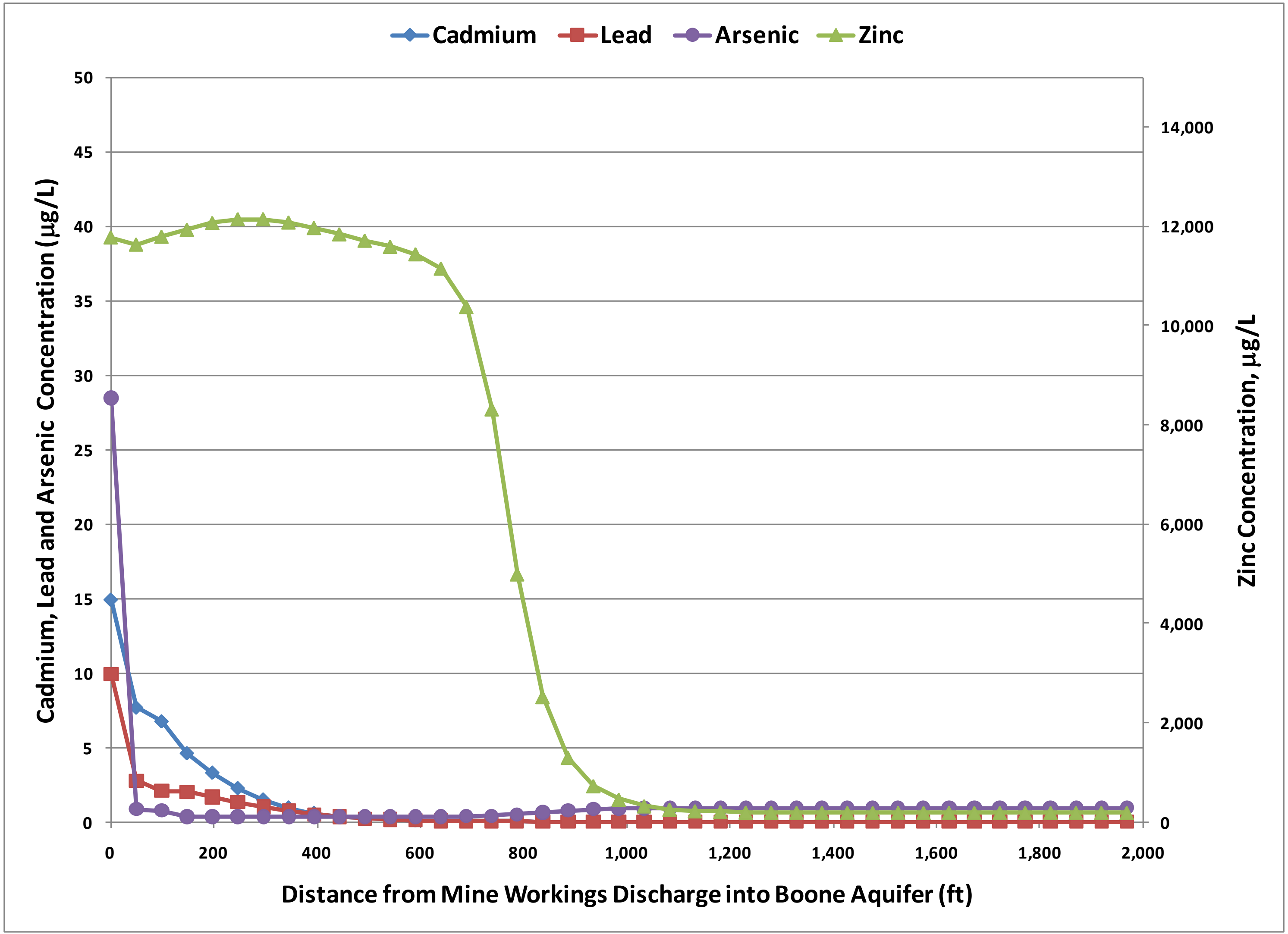
PHAST Model Results
Phase 1: 20 years (~1990)



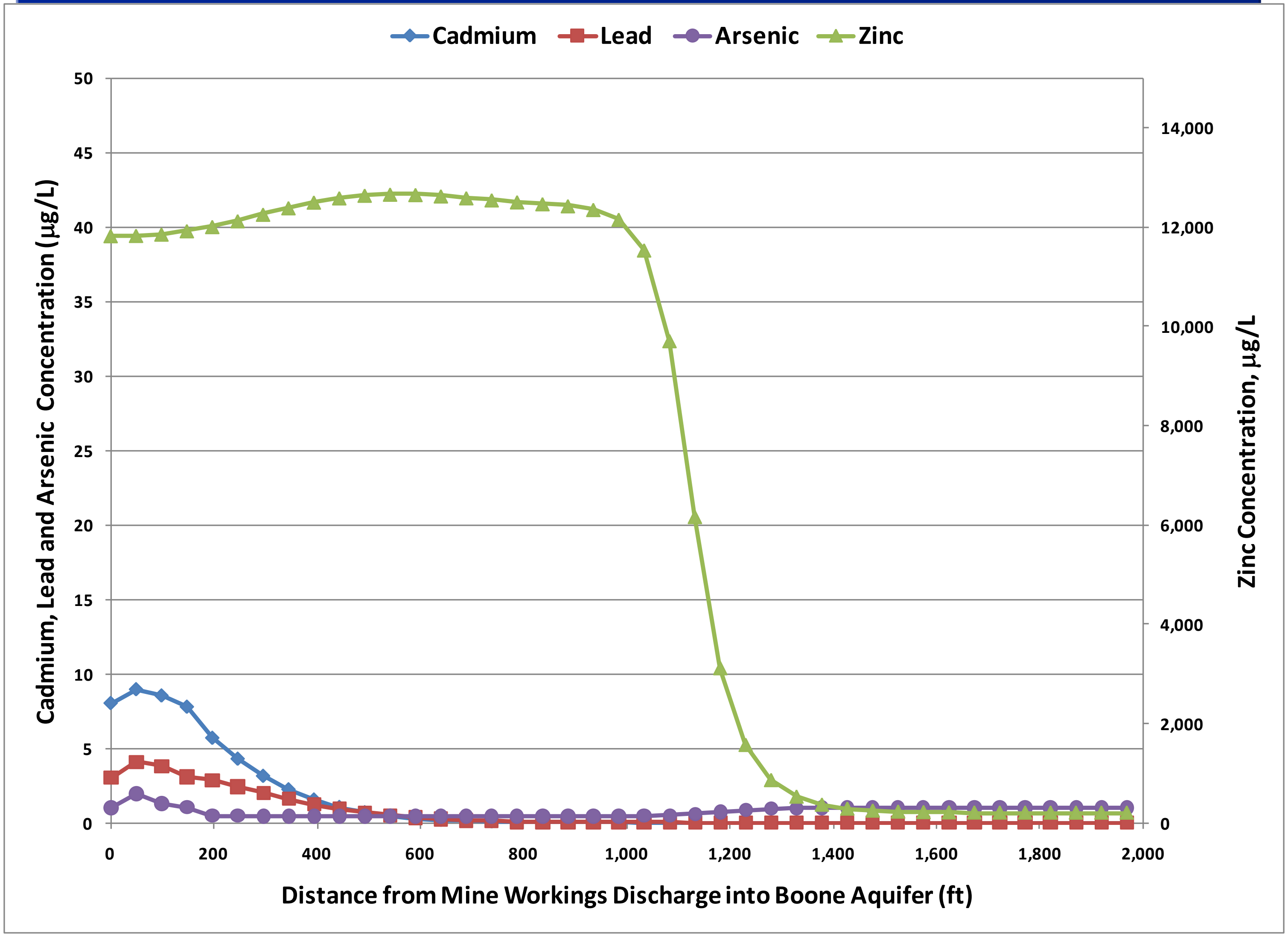
PHAST Model Results
Phase 1: 40 years (~2010)



PHAST Model Results
Phase 2 Sooner: 5 years



PHAST Model Results Phase 2 Sooner: 25 years

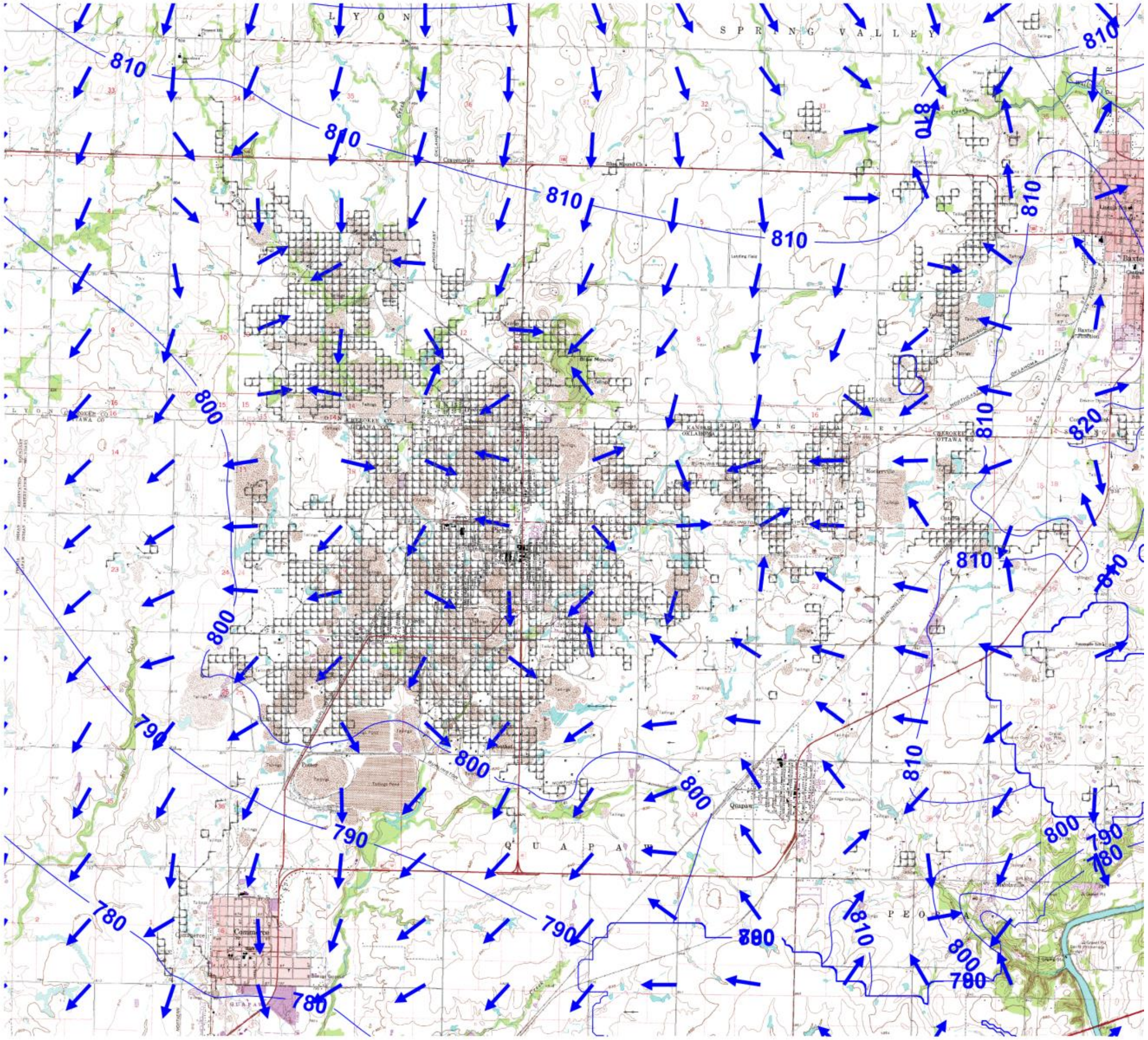


Conclusions: Geochemistry

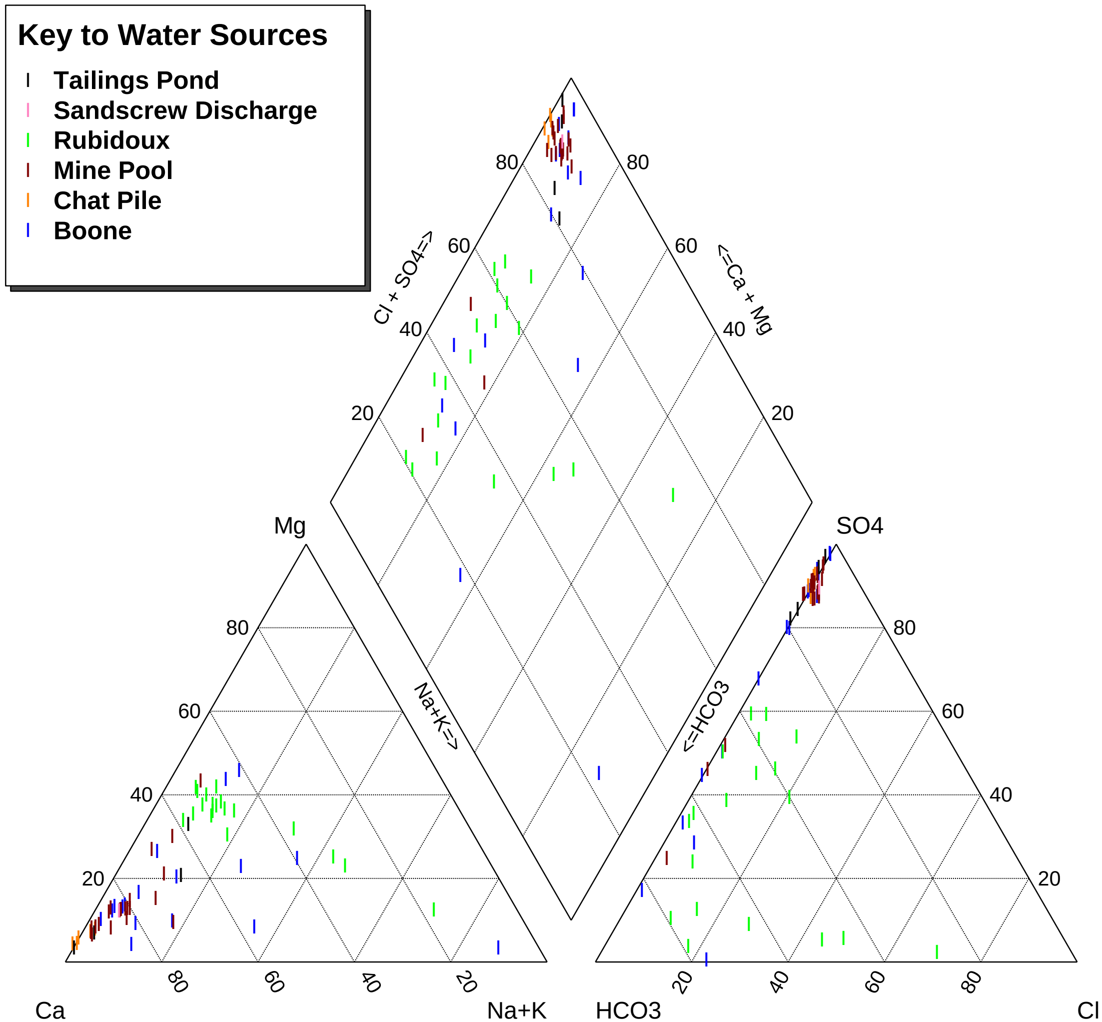
- **Trace metal minerals and salts dissolve during slurry process**
- **Injected slurry temporarily increases metals concentrations in mine pool**
- **Concentrations return to original levels after injection stops (trapped in fines)**
- **Injection expected to have little effect on discharge to Boone Aquifer**
  - Higher concentrations temporary
  - High dilution in mine workings
  - Further attenuation after discharge

Questions?

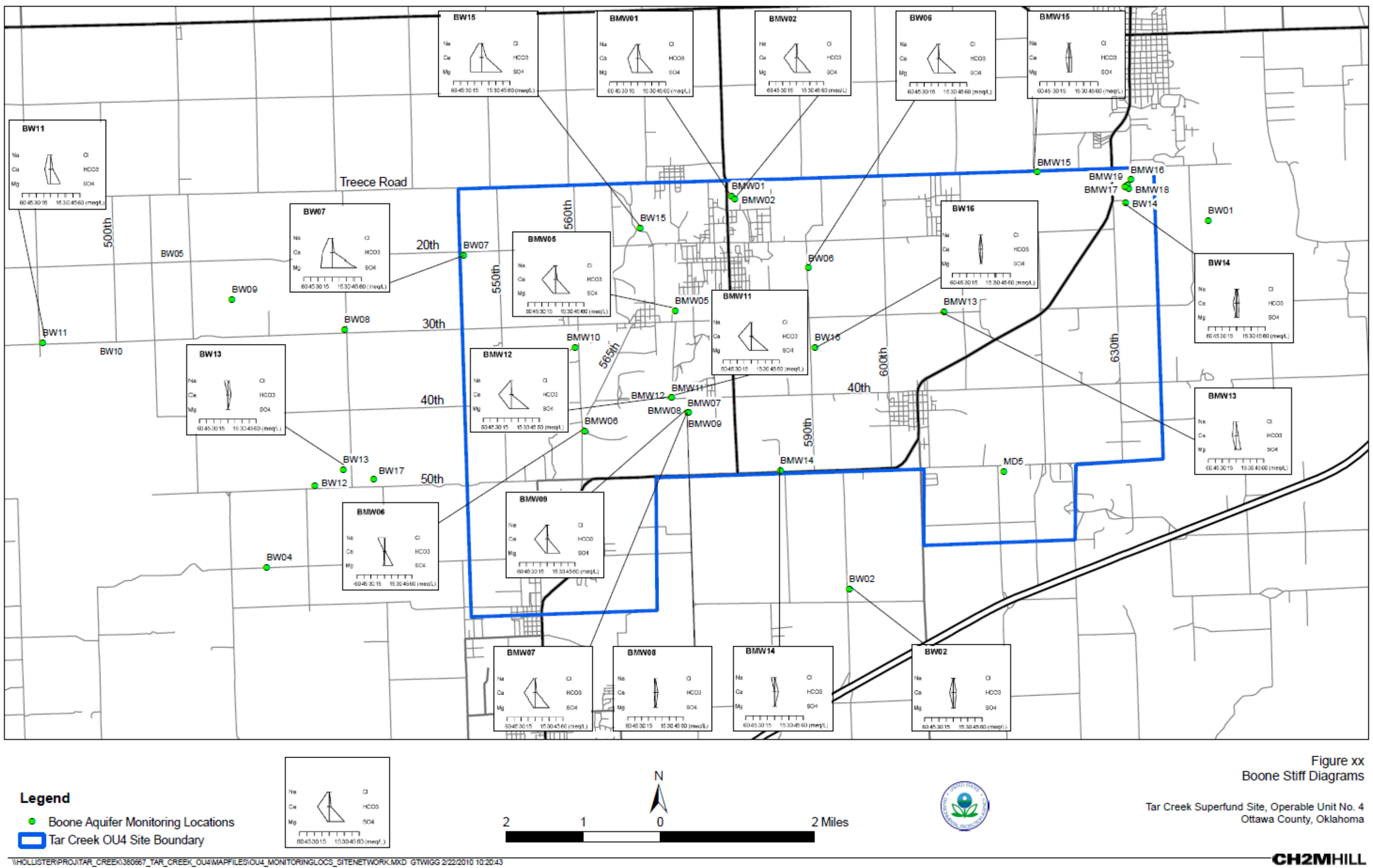
Groundwater Flow Directions



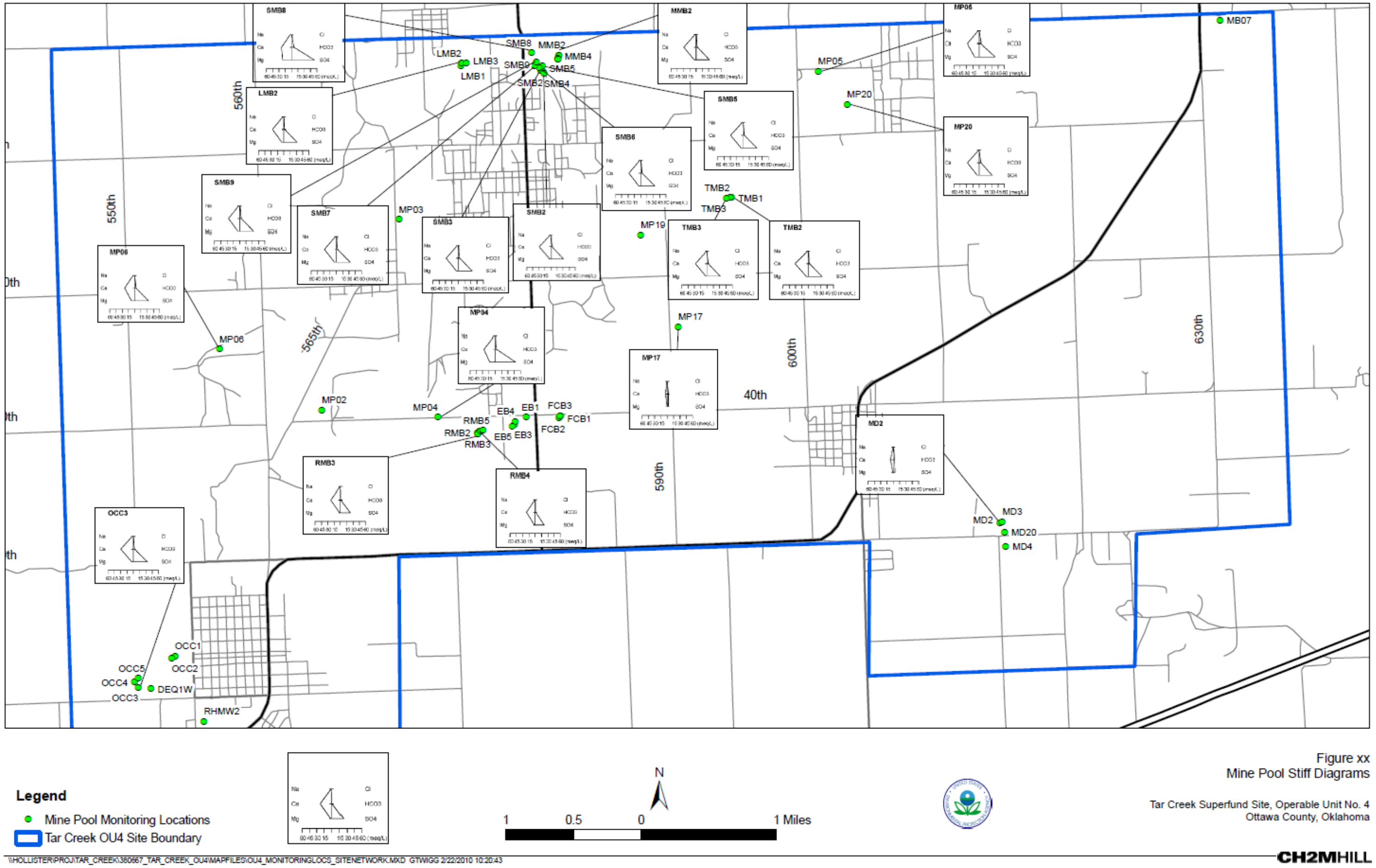
Piper Diagram



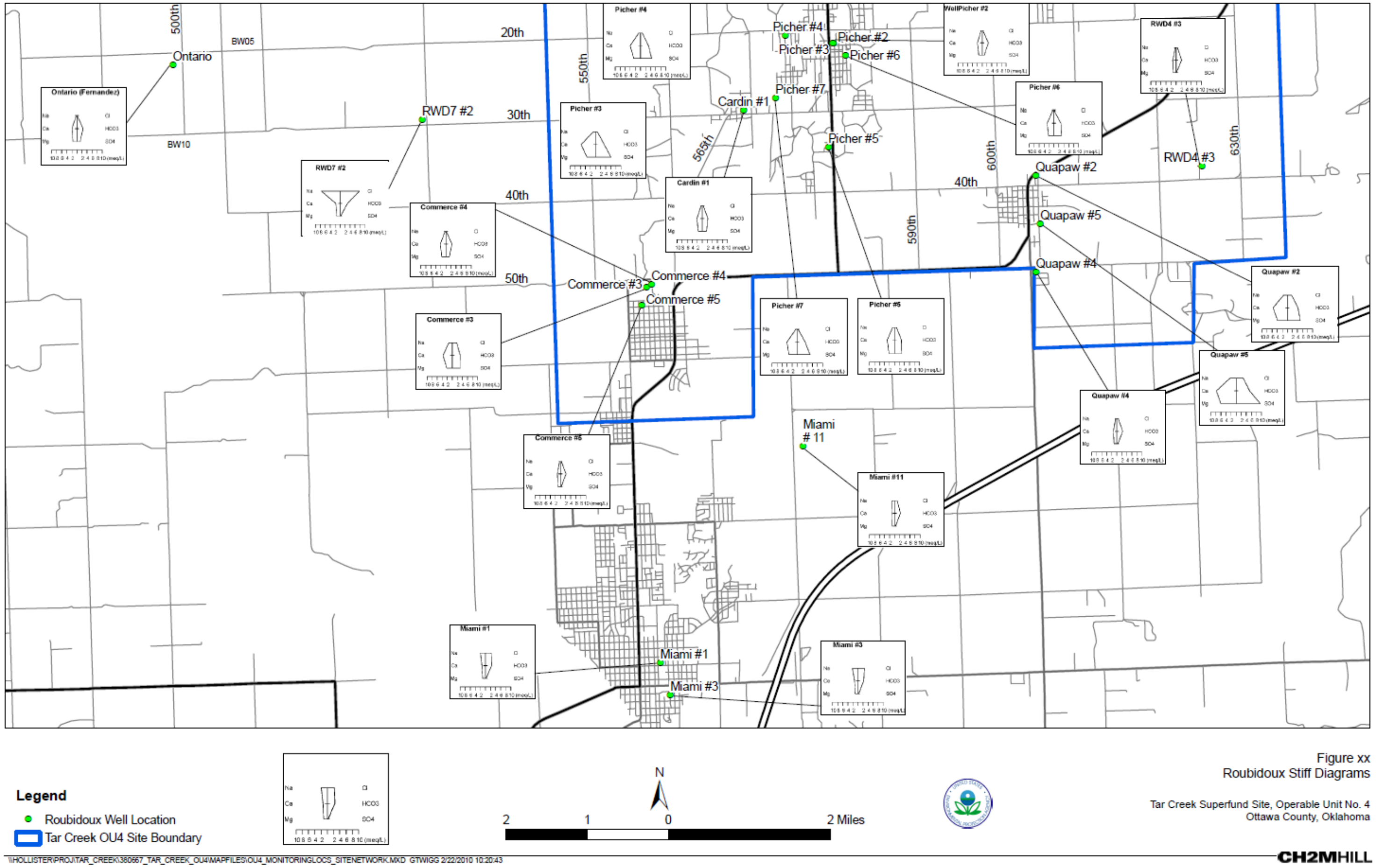
Boone Groundwater Chemistry



Mine Pool Water Chemistry



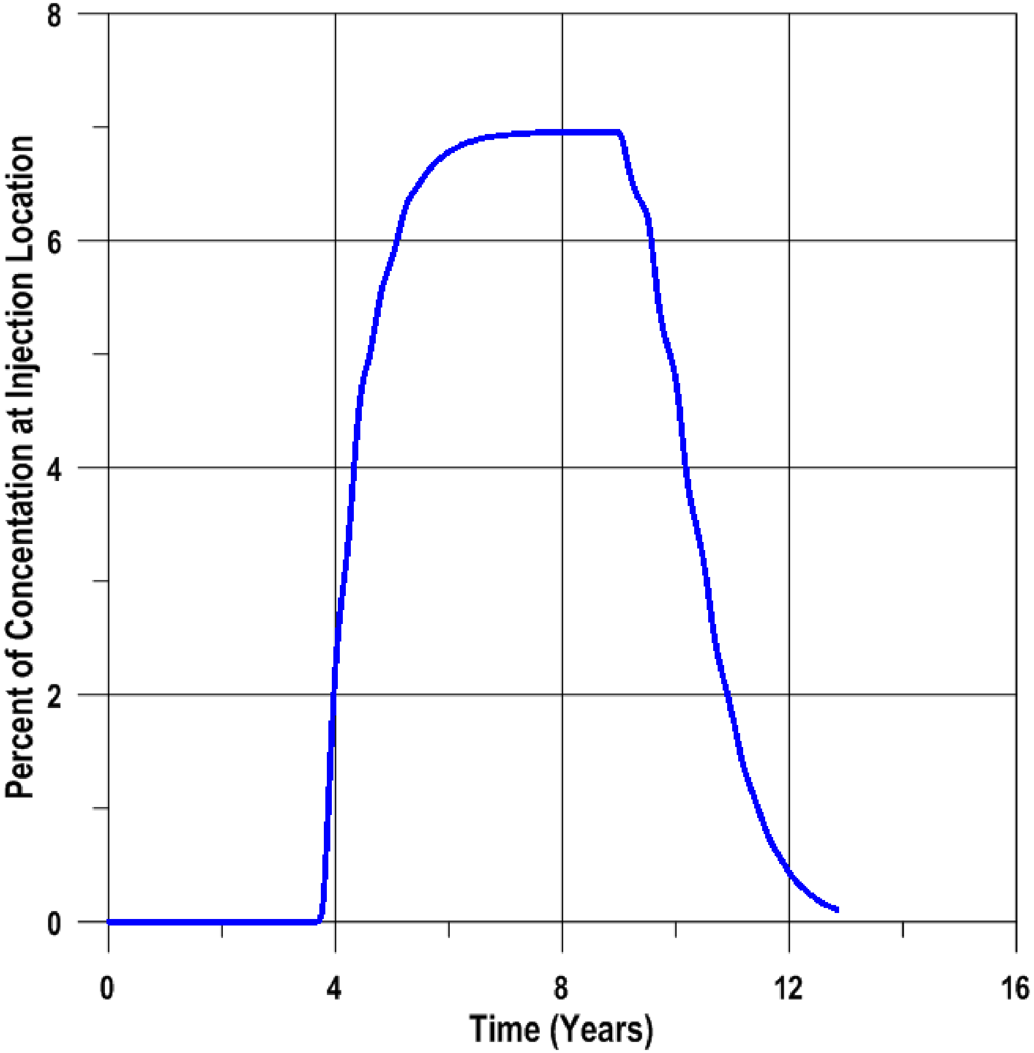
Rubidoux Groundwater Chemistry



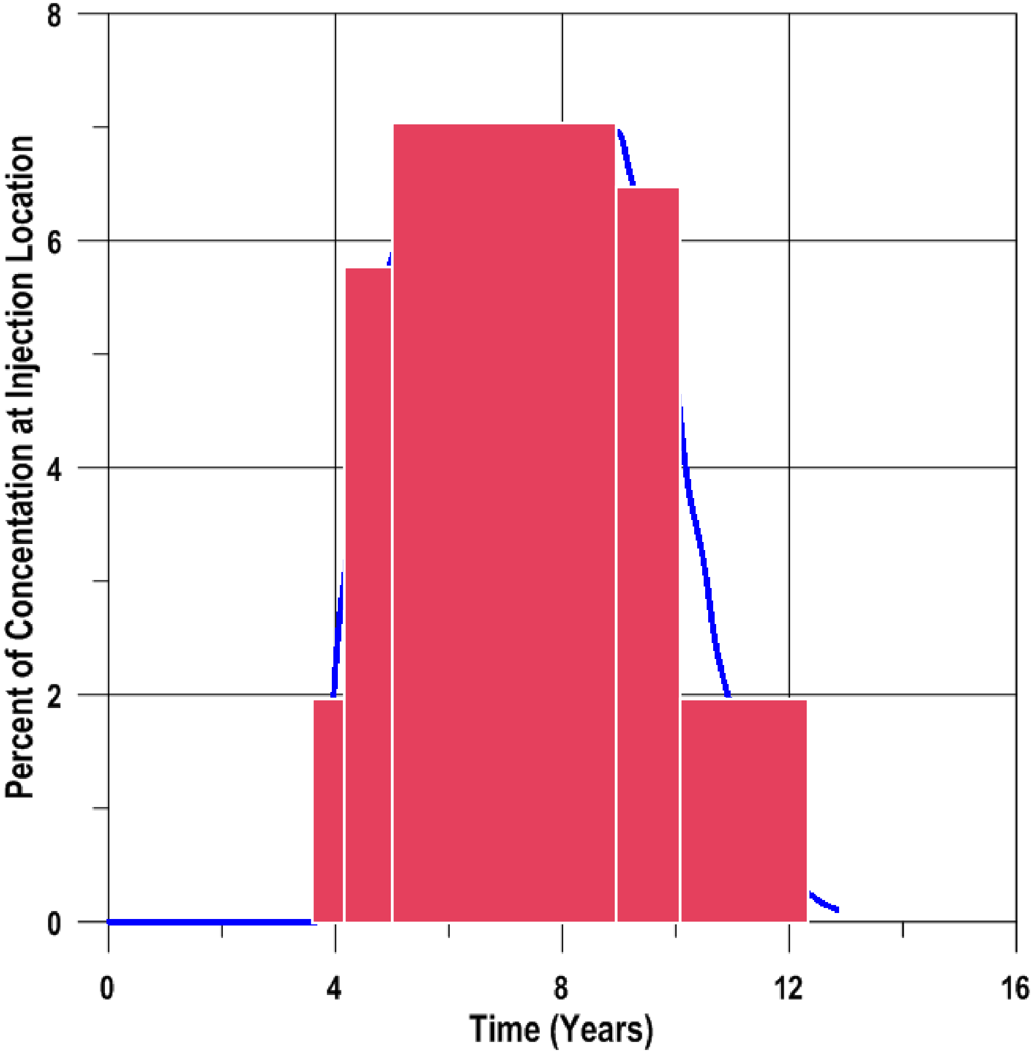
PHAST Model

- Alternative to use of K_d for adsorption by explicitly modeling adsorption of metals to mineral surfaces
- Database contains expressions for adsorption to hydrous ferric oxides, the most common adsorbent
- Can add published expressions for other minerals (carbonates used in this study)
- Measured or assumed mineral concentrations provide more realistic ceiling for adsorption reactions
  - K_d assumes unlimited adsorption capacity

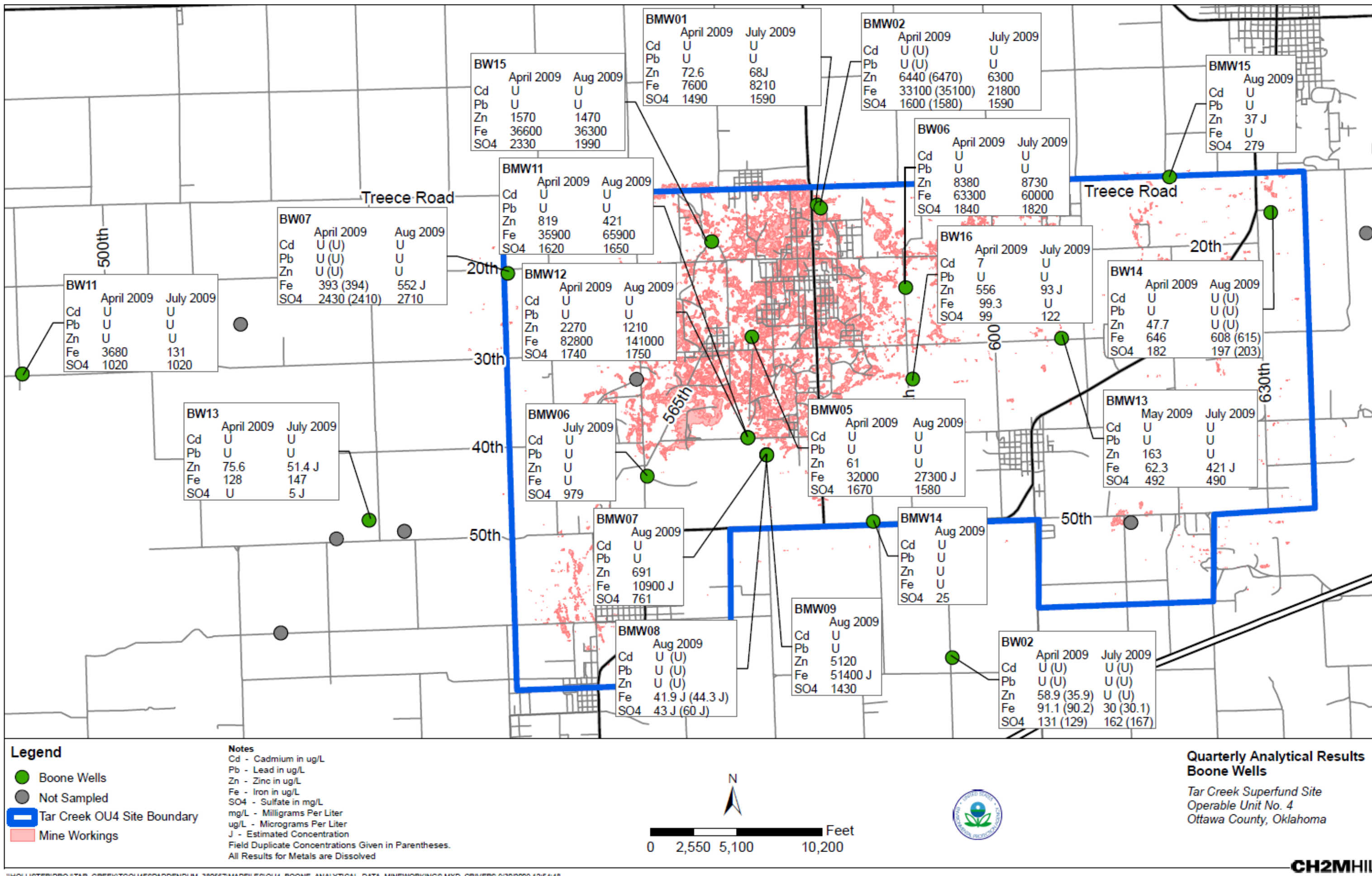
Dilution from Sooner Location



Dilution from Sooner Location



Observed Data: Douthat



Observed Data: Douthat