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Groundwater Monitoring Plan Considerations for Corrective Action Sites

World of Coal Ash

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Overview

Evaluate strategies beyond routine detection monitoring.

Doing the geochemical detective work during assessment
can save time and money
to focus on the right remedy.

Outline

SURVEY

- Issues at Play
- Geochemical Behaviors
- Hydrogeological Settings
- Investigatory Methods

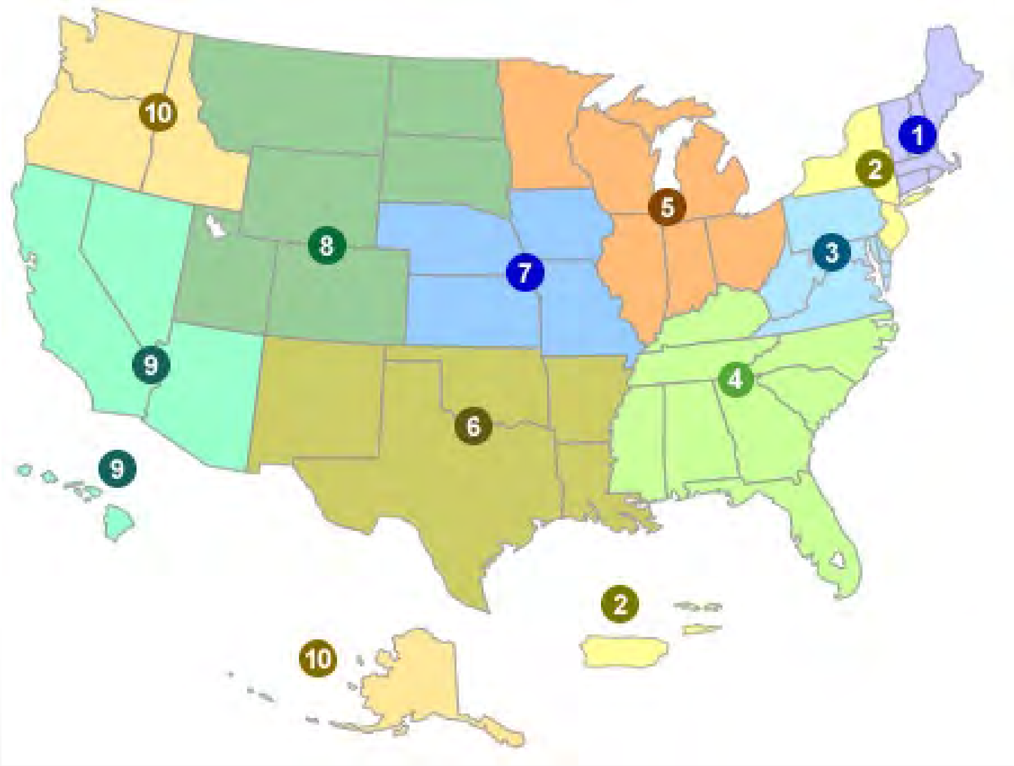
SPECIFIC EXAMPLES

- Considerations for Suspended Solids
- Support of Cobalt Association with Sediment
- Lack of Correlation with Suspended Solids
- Arsenic Source Alternative

SUMMARY & CONCLUSION

- Recommendations

Snapshot Survey of Groundwater Issues in Play



EPA Region	Total CCR Units	Units in Detection Monitoring	Unit in Other Monitoring Status	COPCs
Region 1	1	1	0	
Region 2	7	3	4	**Li**, **As**, **Mo**, Se
Region 3	40	11	29	**Li**, **As**, **Co**, **Mo**, Ba, Se, Ra
Region 4	133	34	99	**Li**, **Co**, **As**, **Mo**, Ra, Be…
Region 5	117	44	73	**Li**, **As**, **Mo**, **Co**, Tl, Se…
Region 6	46	23	23	**Co**, **Li**, Se, **As**, Be, Pb, Tl…
Region 7	61	25	36	**Mo**, **Li**, **As**, **Co**…
Region 8	57	26	31	**Li**, **Mo**, **Co**, **As**, Se, Tl…
Region 9	20	17	3	**Li**, **Co**, **As**, **Mo**, F
Region 10	3	2	1	**Li**, **As**, **Mo**, F

Survey of Geochemical Behaviors

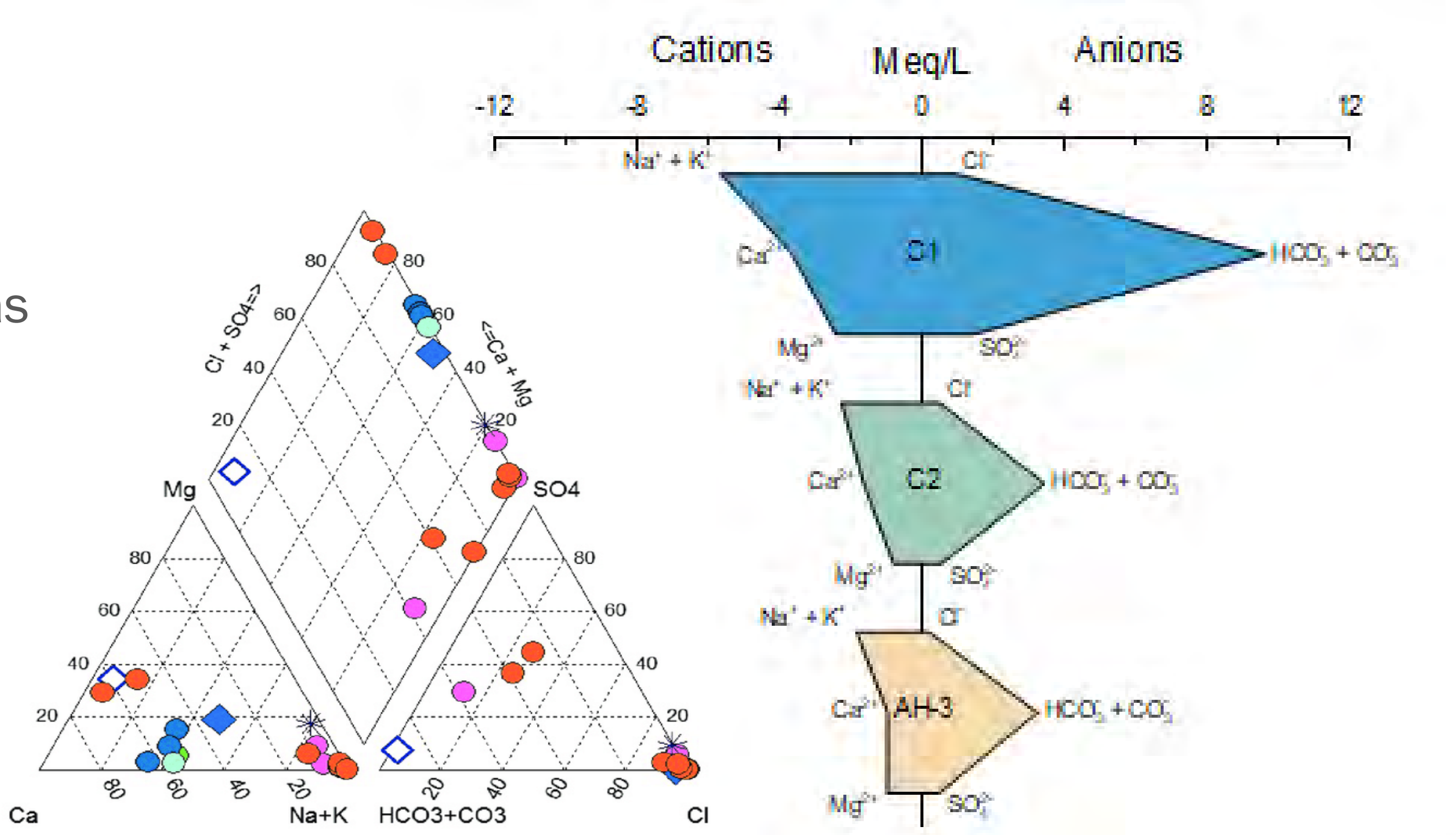
Constituent	pH Sensitive?	ORP Sensitive?	Complexant?	Solubility Controls?	Sorber?	Naturally Occurring (Near Background)
As	Strong	Strong	Strong	Yes, variable	Yes, variable	Yes, variable
Cr	Strong	Strong	Moderate	Yes, variable	Yes, Variable	Yes, variable
Co	Strong	No	Moderate	Yes	No	No
Cd	Moderate	No	Moderate	Yes	Yes	No
Mo	Moderate	No	No	No	No	No
Ba	No	No	No	Yes	No	Yes
Li	No	No	No	No	No	No
F	No	No	No	No	No	Yes

- Green: Geochemical Methodologies – OFTEN helpful
- Yellow: Geochemical Methodologies – SOMETIMES be helpful
- Red: Geochemical Methodologies – RARELY helpful

Investigatory Methodologies

Hydrochemical Facies

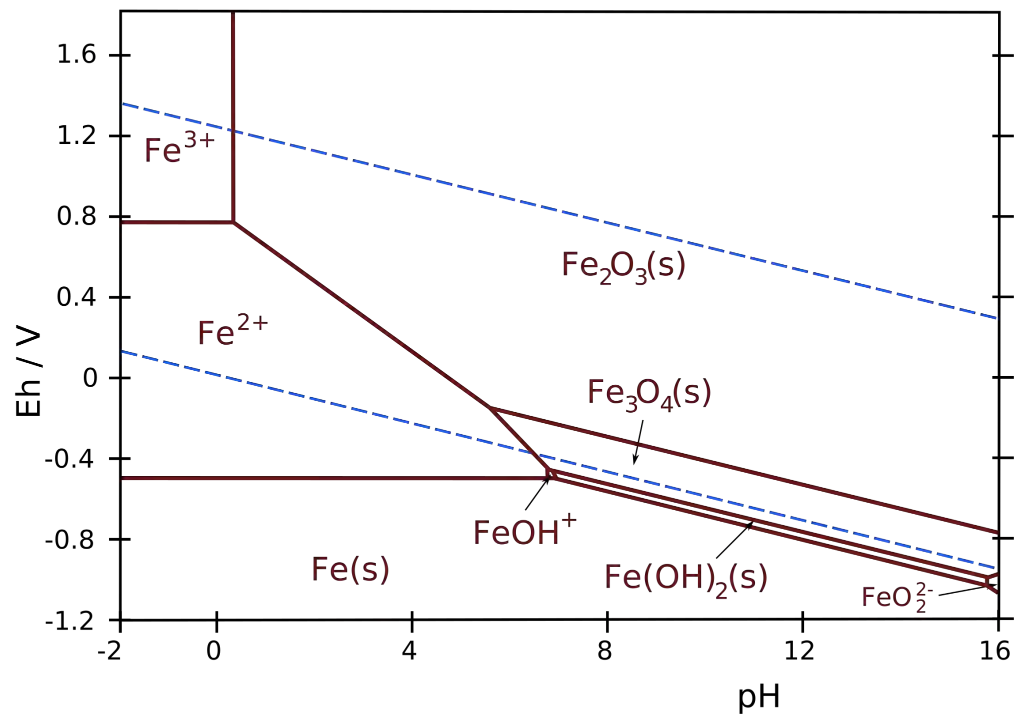
- The concentrations of major cations and anions arise from interactions with solid phases in the porous medium through which groundwater is flowing.
  These ratios can also change with time as the interactions are not always instantaneous.
- This technique looks at major cations and anions to understand provenance.
- They can **help determine** the **degree** to which water that has **contacted CCR** has **impacted groundwater quality**.



Investigatory Methodologies

Redox Sensitivity

- Major, minor, and trace cations may exist in different oxidation states. The geochemical mechanisms that determine fate and transport are often very different depending on oxidation state.
- One technique is to measure ORP (and/or dissolved oxygen) in the field in groundwater along a flow line and calculate the distribution of different species assuming all of the redox couples are in equilibrium.
- A second technique is to directly measure the total species.



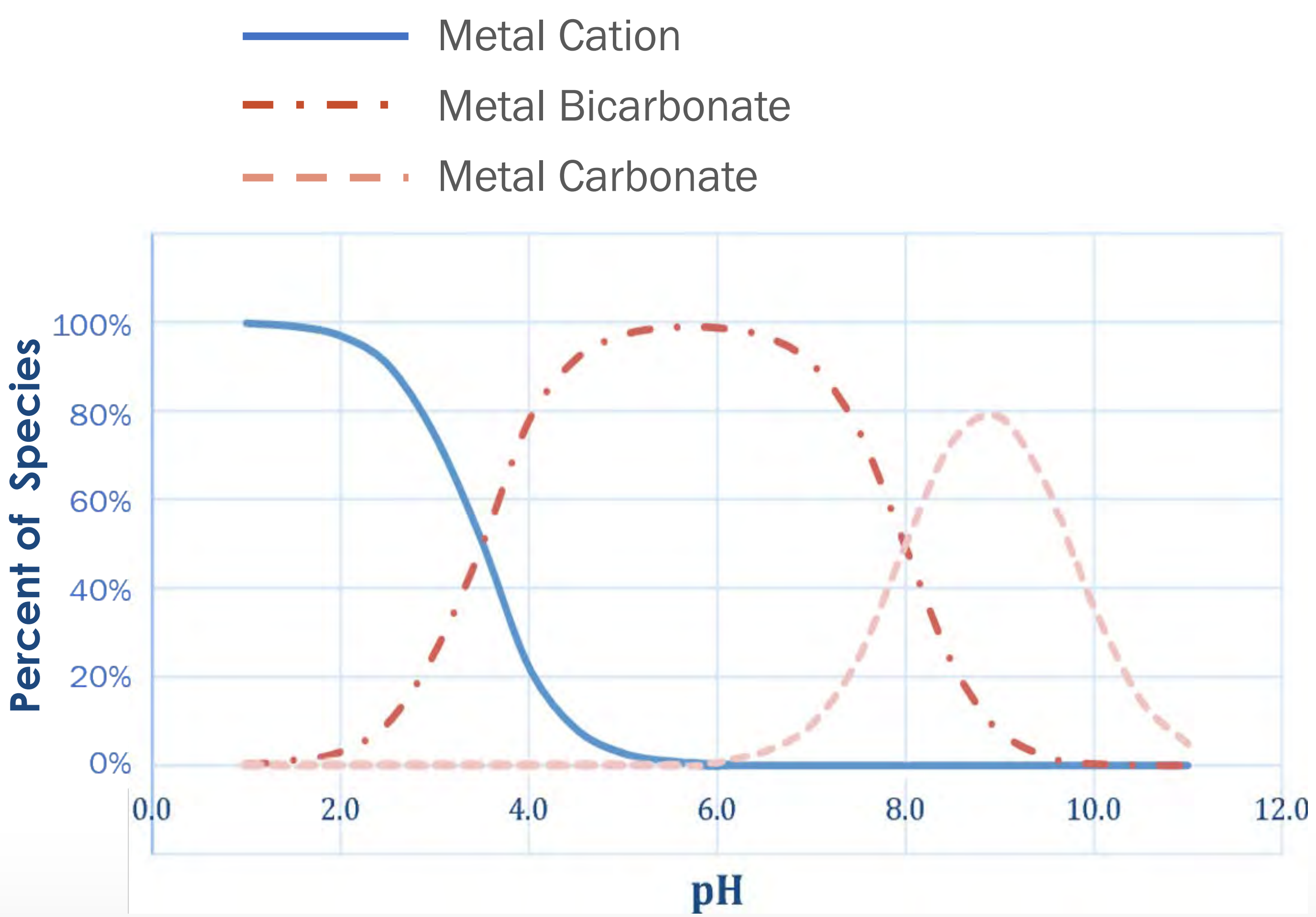
▶ This information can be used **to understand** the **mobility** of **dissolved constituents**.

Investigatory Methodologies

Geochemical Speciation

- Speciation/solubility/ sorption mechanisms also affect fate and transport.
- These are strongly dependent on pH, the solid phase assemblage that exists a long a flow line, and the presence of organic matter in the porous media.

▶ This information can be used **to understand** the **mobility** of **dissolved constituents**.

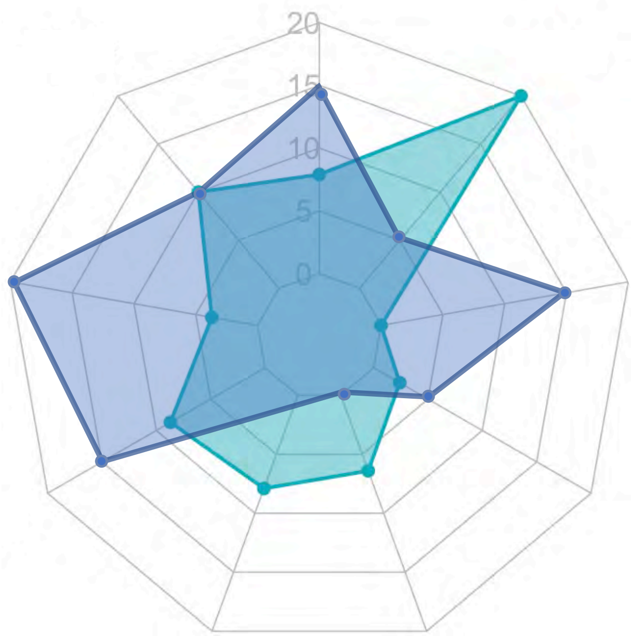


Investigatory Methodologies

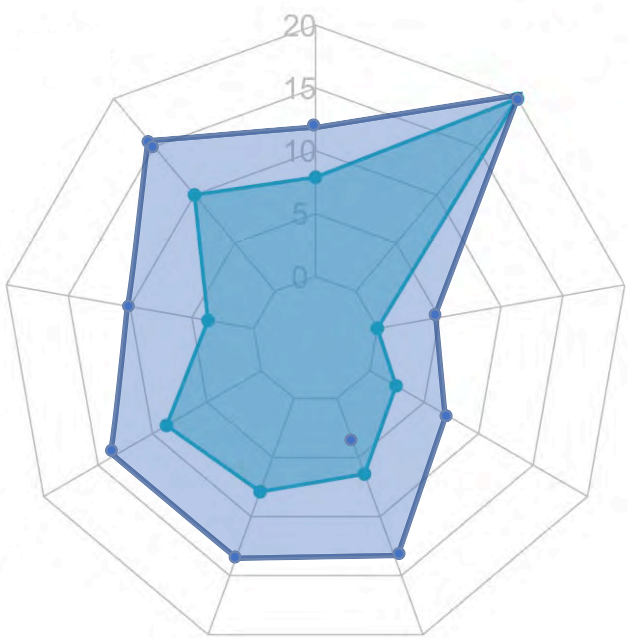
Chemical Fingerprinting

- Source controls on concentrations.
- Conservative tracers and chromatographic separation.
- Ratios and radar diagrams.

These fingerprinting plots can **help** us understand the **evolution** of a **groundwater plume** as it **moves downstream**, or whether there is a plume at all.



Shapes are different illustrating **two different major** element chemistries or differential **separation** along a flow path.



Shapes are similar, illustrating **no differential** separation along a flow path and **a common source chemistry.**

Transition from **Survey** to **Specific Examples**

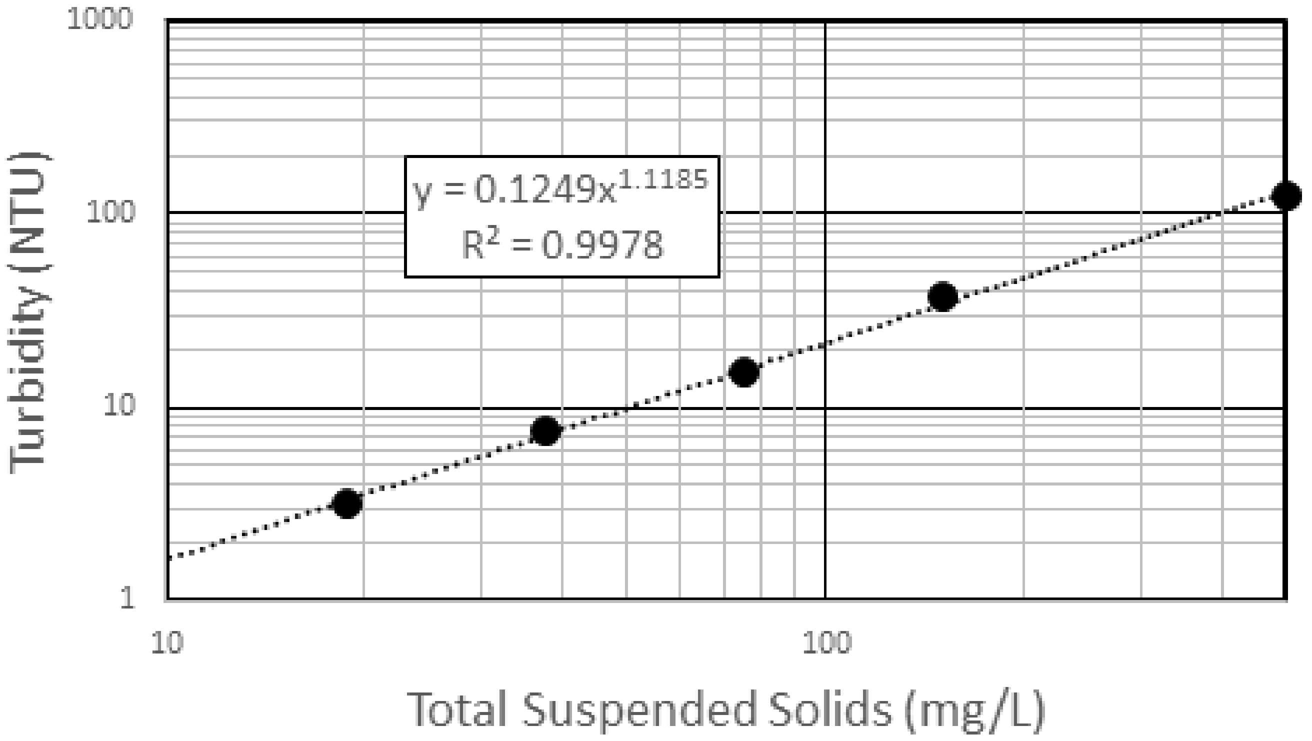
- The preceding materials **surveyed** the characteristics of groundwater monitoring programs at CCR sites and some of the general investigatory methods.

- The following materials provide **site-specific examples** of the uses of these methods and how they can be used to solve specific permitting problems.

- USEPA Guidance (OSWER Directive 9283.1-36) emphasizes the need for studies which "…**directly** demonstrate the occurrence of a particular natural attenuation process at the site…". The same approach is applicable when demonstrating alternate sources of constituent releases.

Considerations for Suspended Solids

- Suspended solids present even at low turbidity.
- Unfiltered sample acidification (preservation) releases adsorbed trace elements.
- Limited transport of particulates at very low water velocity in porous media.
- Element-specific.



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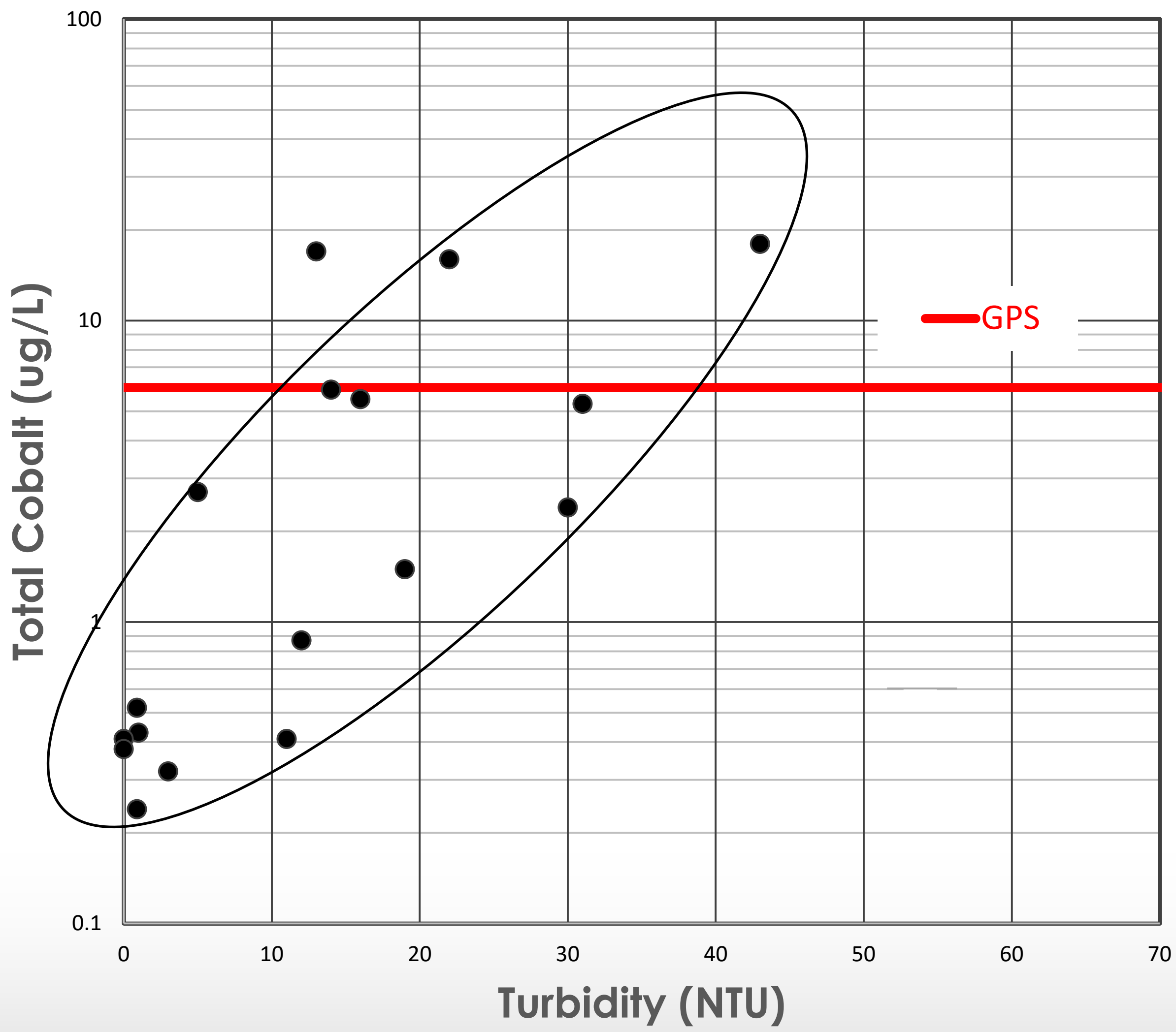
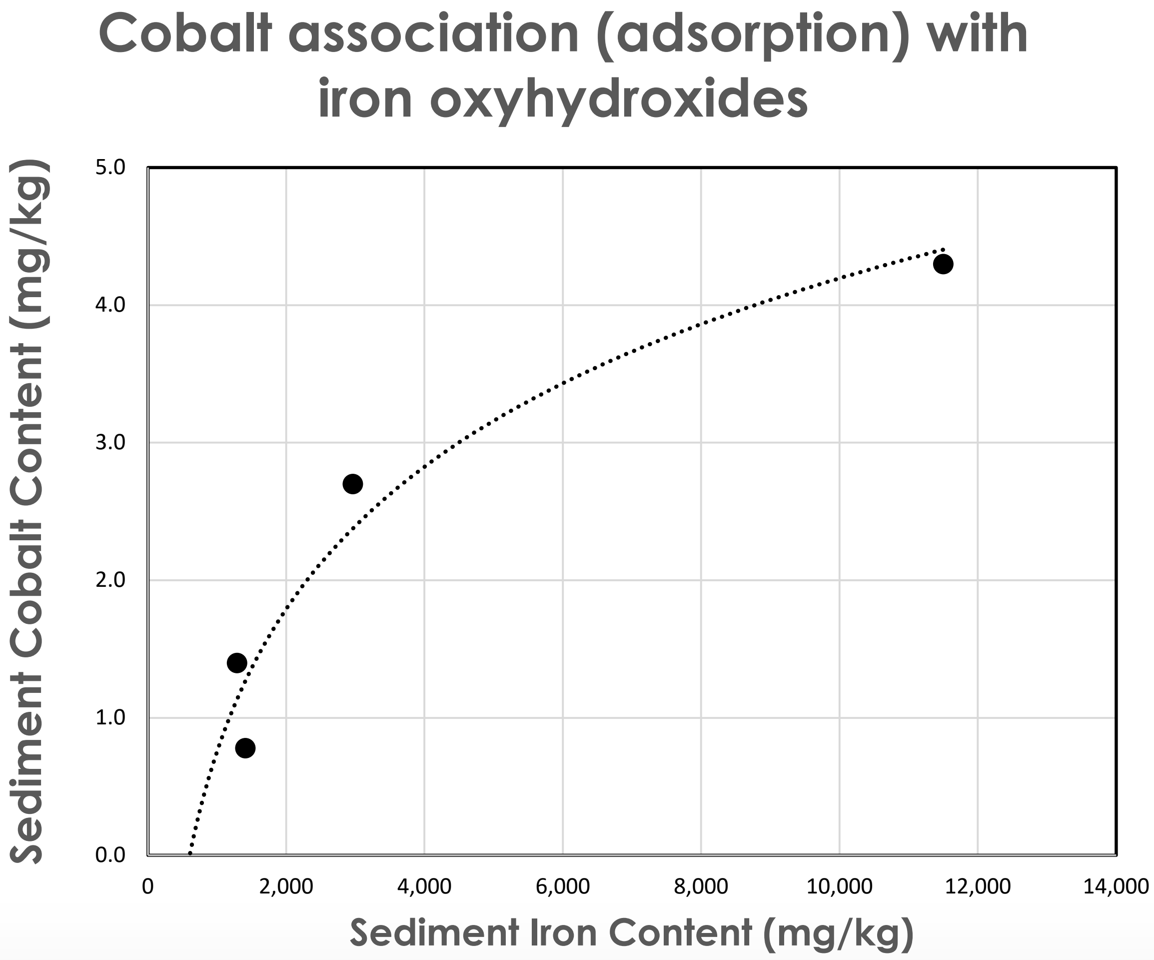


Support of Cobalt Association with Sediment



Suspended sediment analyzed for iron and cobalt:

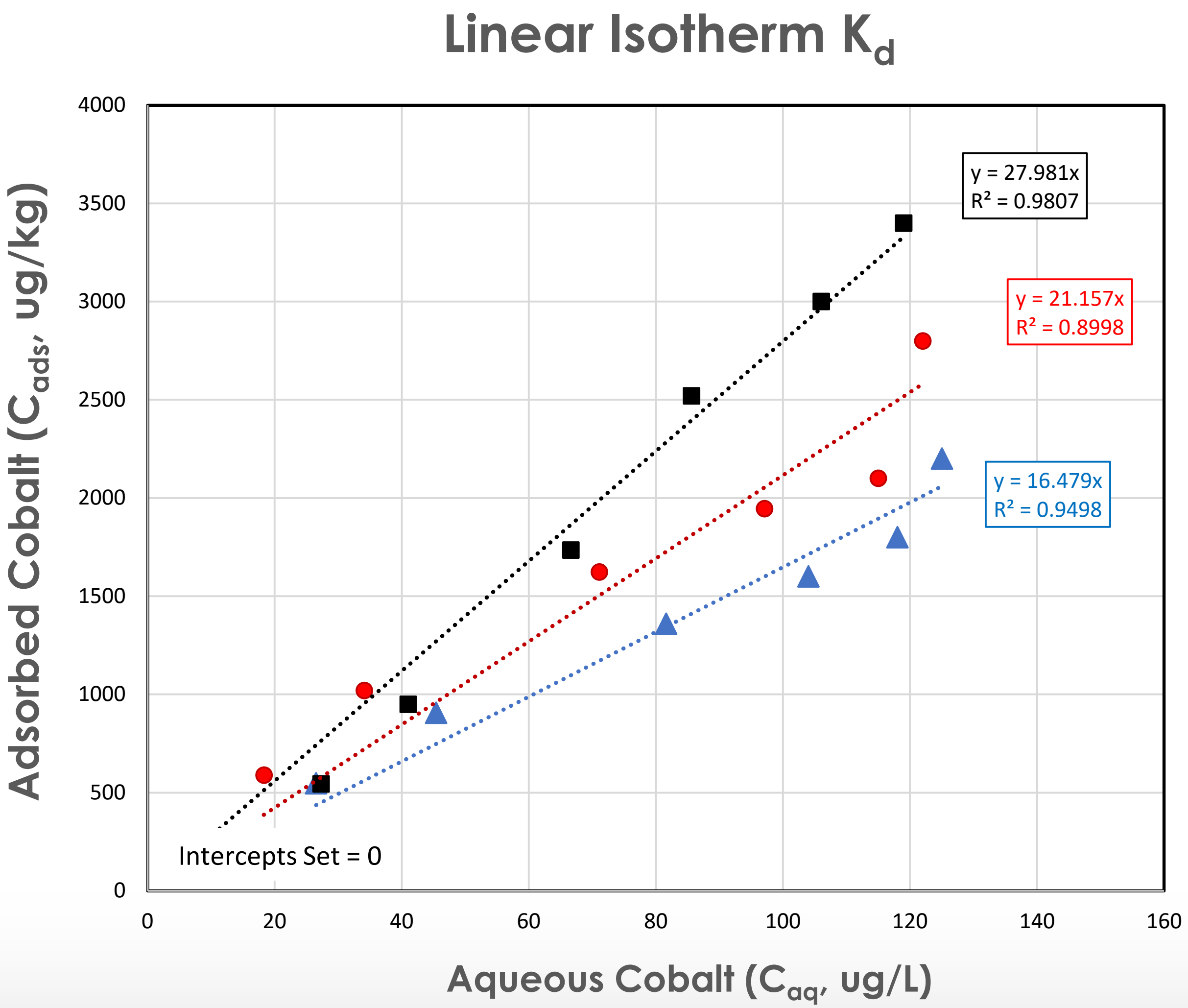
- Cobalt concentration is positively correlated with iron concentration.
- Identifies cobalt adsorption to iron oxyhydroxides.

Sometimes you need to sample and analyze **aquifer solids** as well as groundwater.

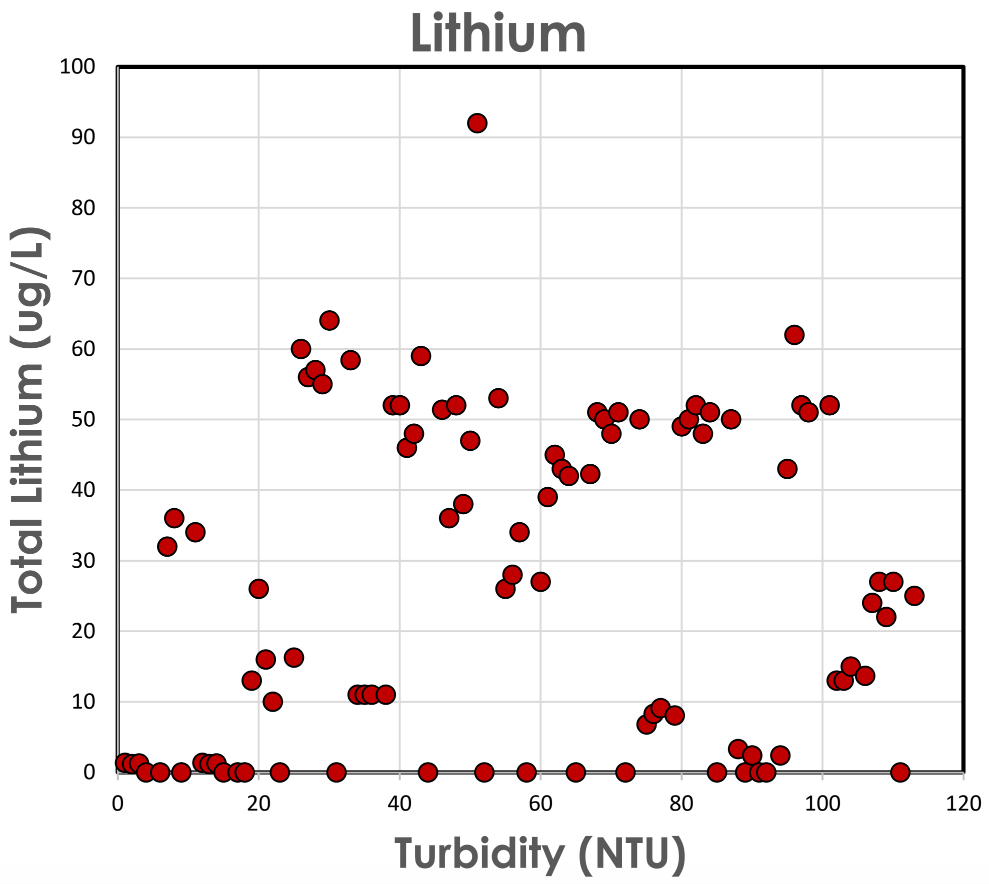
Support of Cobalt Association with Sediment

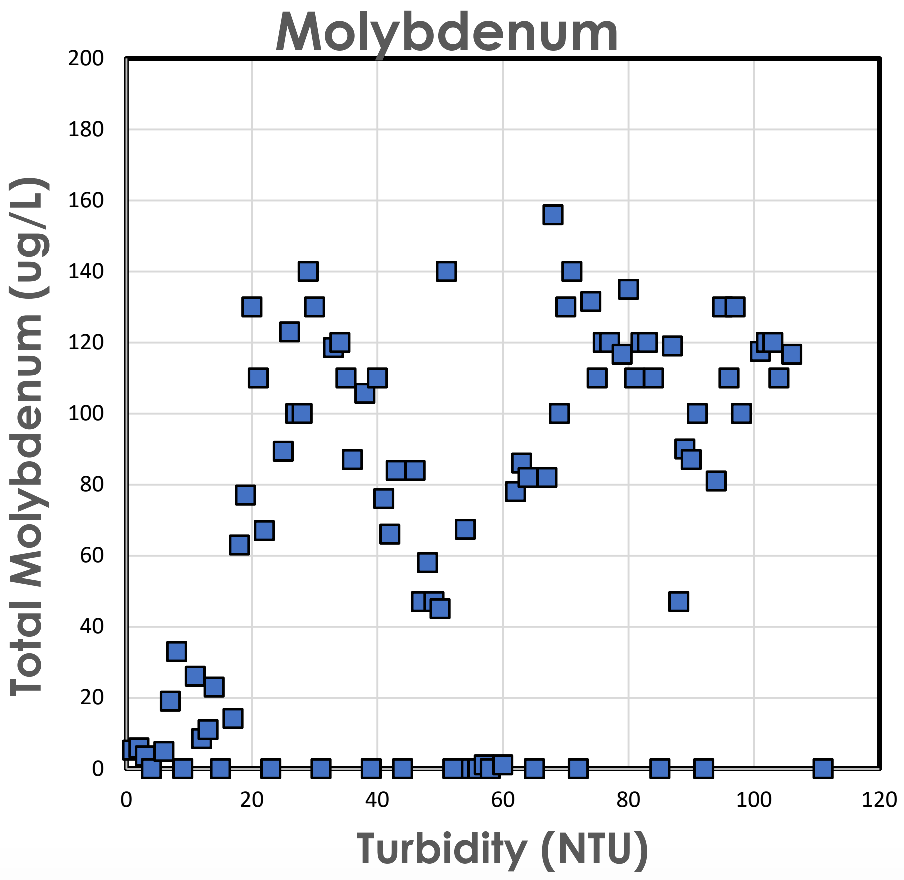
- Adsorption to sand aquifer solids is a key driver for natural attenuation.
  - Aqueous concentrations up to 120 ug/L fit linear isotherm.

>95% of cobalt irreversibly adsorbed – makes **MNA an acceptable remedy** in this case.

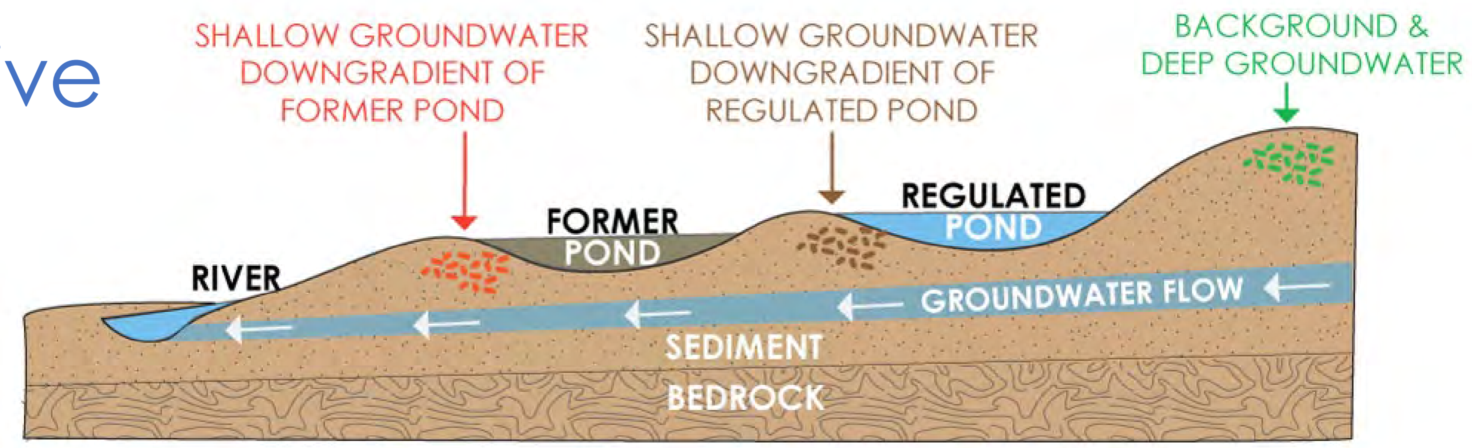


Lack of Correlation with Suspended Solids



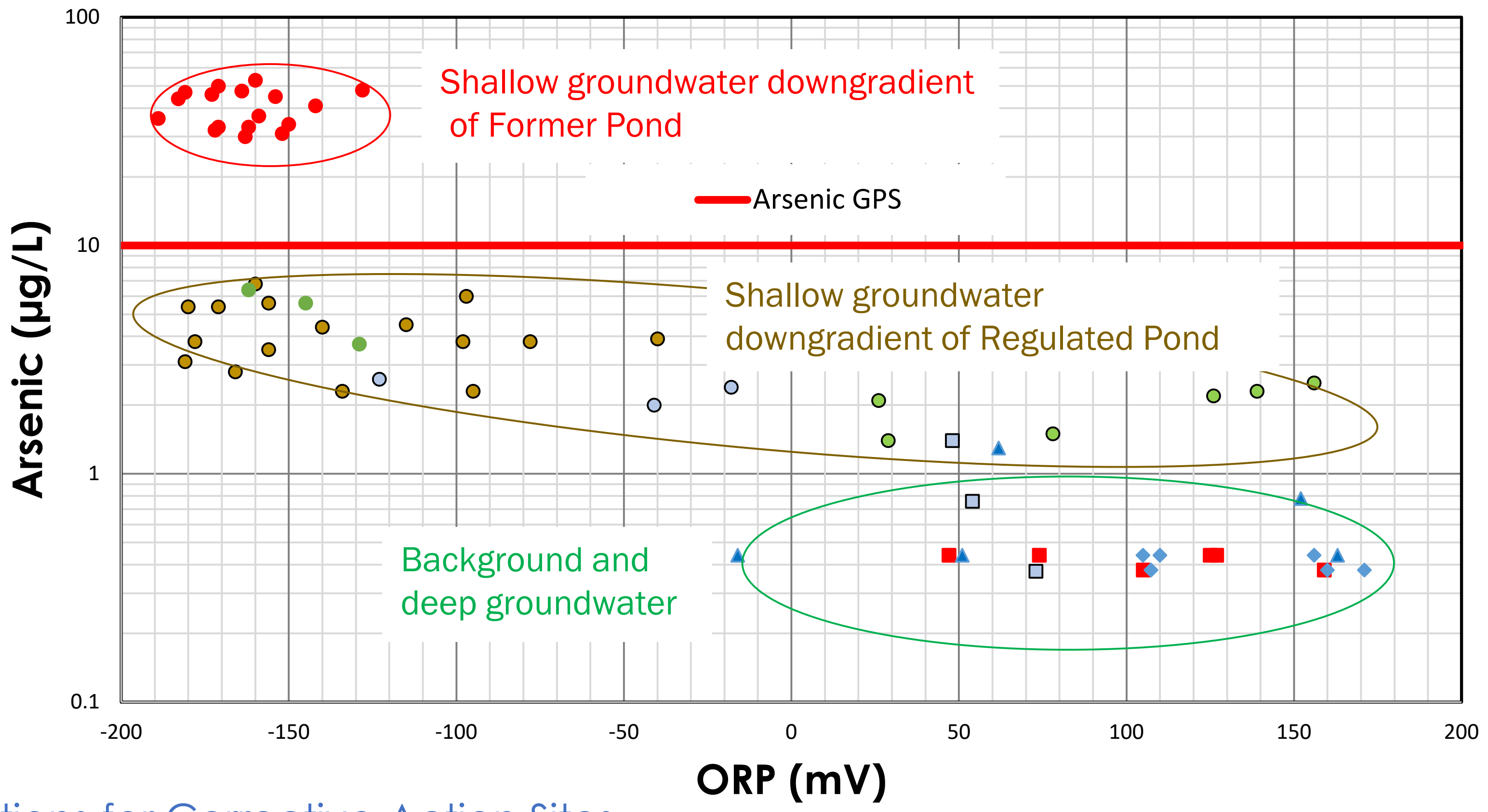


Arsenic Source Alternative



- Does downgradient arsenic originate with CCR Units?
- pH from 7 to 8 SU not helpful but ORP clearly defines three chemistries.
- Geology upgradient of Former Pond varying glacial drift … downgradient is black organic-rich silt/sand. Possible fill material placed to make Former Pond Berm?

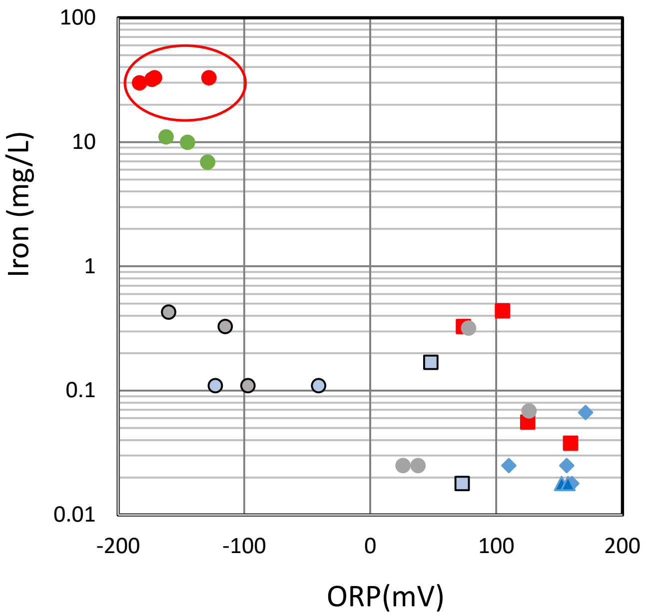
▶ **So what is happening?**

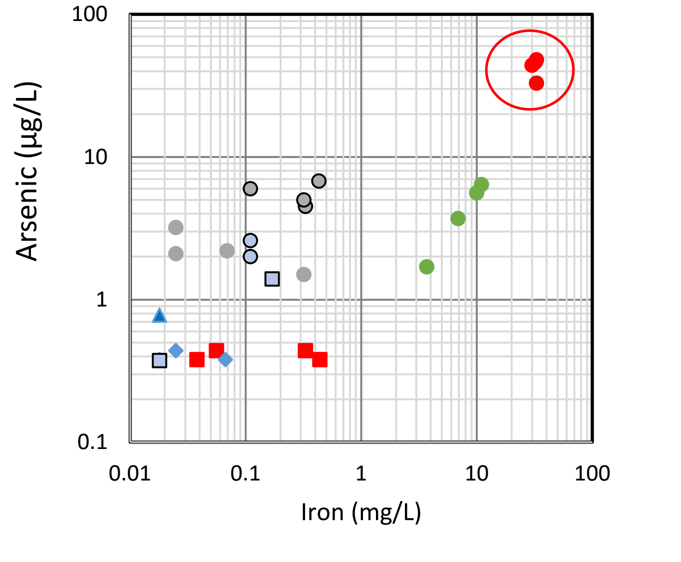


Arsenic Source Alternative (continued)

- Organic-rich sediments generate low ORP.
- Low ORP dissolves iron oxyhydroxides that have absorbed/co-precipitated arsenic (upper-left chart).
- Arsenic released as the iron oxyhydroxides dissolve (lower-right chart).

➤ CCR Unit **not the source!**





Summary & Conclusions

- **Corrective Actions** may need to address **several** constituents and issues.
- **The fate and transport** of some elements are **controlled by** one or more geochemical processes in aquifers:
  - **Processes**: **Precipitation and Solubility** and **Complexation and Adsorption.**
  - **Controlling factors**: pH, ORP, valence state, counter ions, suspended solids, matrix solids.
  - **Weak control**: Ba, F, Li, Mo.
  - **Strong control**: As, Cd, Co, Cr.
- **Monitored natural attenuation** requires a demonstrated understanding of the underlying processes.
- Requires **site-specific testing** beyond the minimum CCR parameter list.

Recommendations

- The Appendix III and IV lists of parameters do NOT contain all the aqueous species necessary to diagnose and/or treat exceedances in groundwater. Consider adding:
  - Field measurements (e.g., turbidity, ORP) to help understand the behavior of redox-sensitive constituents and potential constituent adsorption.
  - Major and minor cations and anions when the origin of aqueous constituents of concern is in question.
  - Key trace metals that may control aqueous fate of target analytes.
  - Don’t forget the potential role aquifer solids may play in the fate of aqueous target analytes.