Groundwater Monitoring Plan Considerations for Corrective Action Sites

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KEYWORDS: coal combustion residual (CCR), groundwater monitoring, supplemental parameters, assessment monitoring, corrective action monitoring

ABSTRACT

The Federal Coal Combustion Residual (CCR) Rule requires sampling of a set of seven Appendix III detection monitoring parameters and fifteen Appendix IV assessment monitoring parameters. Experience has shown that effective assessment and corrective action groundwater monitoring programs go beyond the prescribed parameter list in the Rule. From the time a site enters the assessment monitoring stage, a fluid data collection program tailored to the site's geology, hydrogeology, contaminants, and landfill or impoundment design, can provide long-term benefits beyond just checking the monitoring compliance box.

During assessment monitoring, supplemental monitoring parameters added to the program, often at a relatively low cost, can help differentiate potential groundwater impacts from the site from naturally occurring constituents and other sources of impacts to groundwater, keeping the site out of corrective action.

At the stage of assessing corrective measures or selecting a remedy, supplemental monitoring parameters can aid in the development of the site conceptual model, support evaluation of monitored natural attenuation, and/or provide background for feasibility assessment for active groundwater remediation approaches.

In this paper, we provide strategies for groundwater monitoring plans that can be tailored to the specific characteristics of a CCR site, supporting updates to the site conceptual model, informing choices of remedial alternatives, and adjusting the monitoring program to keep site evaluation and corrective actions on track.

INTRODUCTION

In early 2015, the United States Environmental Protection Agency (EPA) established new requirements for groundwater and management of Coal Combustion Residual (CCR) surface impoundments and landfills, generally known as the CCR Rule. The CCR Rule identifies CCRs as solid waste under Subtitle D of the Resource Conservation and Recovery Act (RCRA). The CCR Rule is designed to reduce the risk of failure of CCR landfill or surface impoundment, protect groundwater, provide operating criteria for the management of CCR units, and establish national guidelines for CCR unit closure. The CCR Rule requires power plants to provide information to the public regarding the community impacts and the disposal of CCRs in a transparent manner.

The CCR Rule is applicable to both existing and new CCR landfills and surface impoundments including lateral expansion of any existing units. The CCR rule differs from many current state regulations for CCR management at landfills and impoundments, and from state regulations for groundwater quality management near CCR facilities.

The Water Infrastructure Improvements for the Nation (WIIN) Act was enacted in 2016. Specifically, Section 2301 of this Act allows States to develop and submit a CCR permit program to EPA that is, at a minimum, as protective as the federal CCR rule. EPA can approve the program either in whole or in part and, once approved, the State permit program will operate in lieu of the federal CCR rule. These State permit programs must be reviewed by EPA at least once every 12 years or as warranted in certain situations. Currently, Oklahoma, Georgia, and Texas are the only states with approved State permit programs.

The CCR Rule is based on an antidegradation approach to protecting groundwater quality. Regulated unit background water quality is established by measuring constituent concentrations in unimpacted groundwater monitoring wells at the unit. The unit starts out in routine detection monitoring. The concentrations of seven constituents are periodically measured and compared to the site or well background. In the event of a statistically significant increase (SSI) above background for one or more of these Appendix III constituents, the site transitions to assessment monitoring. The minimum constituent list is expanded to include the fifteen Appendix IV parameters in assessment monitoring. Assessment monitoring does not necessarily indicate a particular contamination issue with a regulated unit, but rather is designed to evaluate whether any Appendix IV parameter is present at a statistically significant level (SSL) above the established Groundwater Protection Standard (GPS). If a parameter is determined to be at an SSL above the GPS, then further study is completed to evaluate the origin of the exceedance and whether it is attributable to a regulated unit. In the event that an SSL above the GPS for one or more well/parameter pairs is attributed to a regulated unit, then corrective action may be necessary, and information will be required to select, design, and implement a remedy.

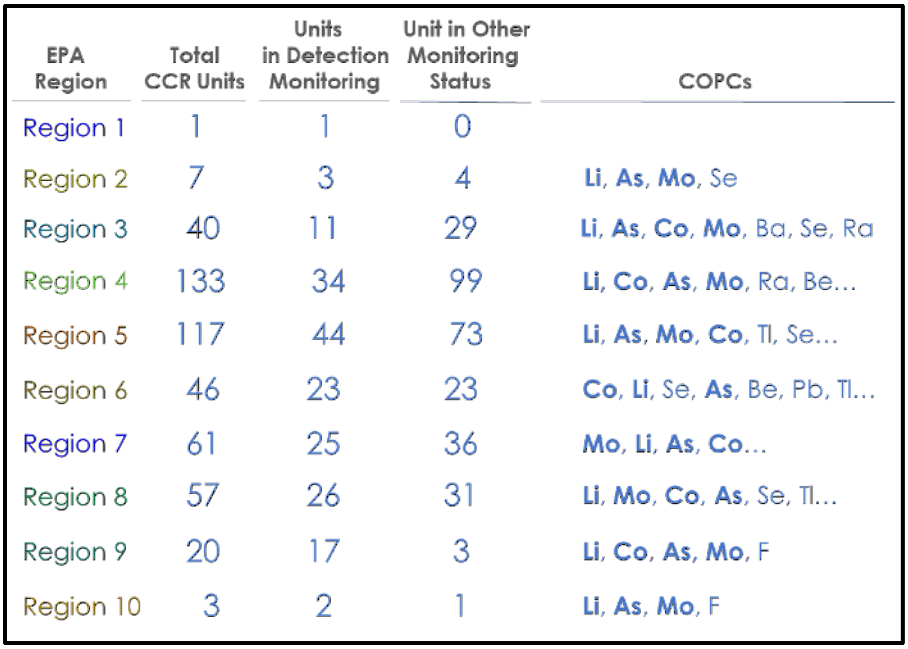
During assessment monitoring, supplemental monitoring parameters added to the program, often at a relatively low cost, can help differentiate potential groundwater impacts from the regulated unit from naturally occurring constituents and other sources of impacts to groundwater, keeping the unit out of corrective action. At the stage of assessing corrective measures or selecting a remedy, supplemental monitoring parameters can aid in the development of the site conceptual model, support evaluation of monitored natural attenuation, and/or provide background for feasibility assessment for active groundwater remediation approaches.

CCR RULE IMPLEMENTATION SNAPSHOT AND KEY PARAMETERS

The CCR Rule is national in scope. Following the implementation of the Federal CCR Rule, the EPA developed a publicly available database of CCR facilities from around the country that post their CCR rule compliance information. The facilities are organized alphabetically by State. Individual websites for each facility can be accessed through the EPA website provided below:

https://www.epa.gov/coalash/list-publicly-accessible-internet-sites-hosting-compliance-data-and-information-required

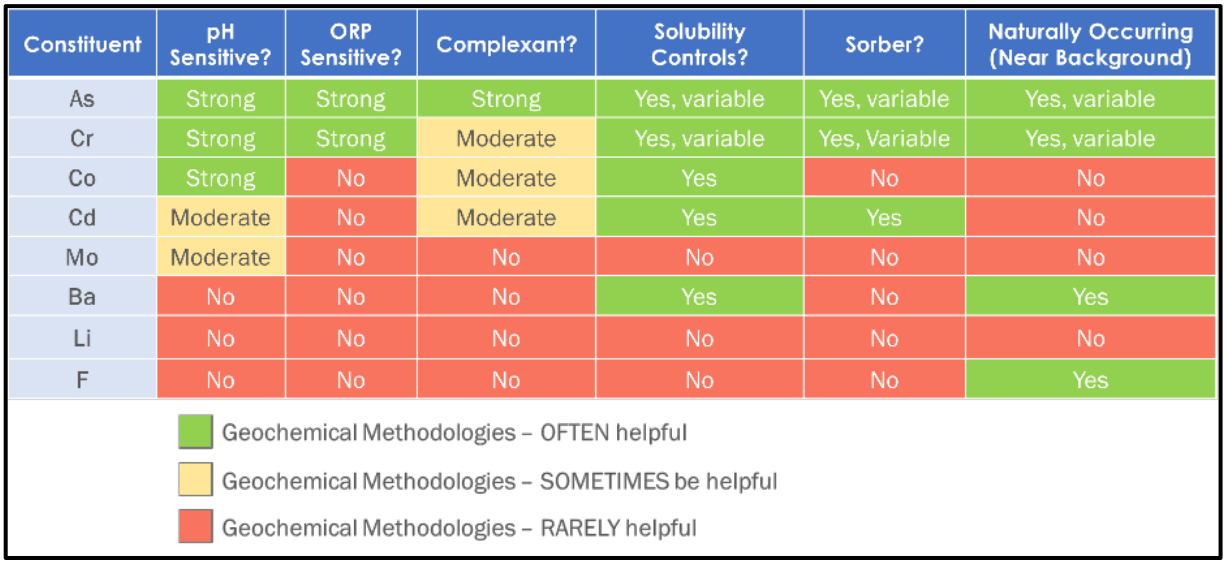
A team of SCS Engineers scientists reviewed each facility's website to summarize CCR unit status and parameters with GPS exceedances based on EPA region (Table 1). All of the EPA Regions have at least one CCR-regulated unit. All EPA Regions except for EPA Region 1 have at least one regulated unit in assessment or corrective action monitoring. Of the 485 regulated units we examined, about 299 of them, or 62 percent, were not in routine detection monitoring. EPA Regions 3 and 4 had almost 75 percent of their regulated units in assessment or corrective action monitoring programs. It is apparent that assessment and corrective action monitoring are not infrequent and they consume a significant proportion of the resources associated with groundwater monitoring performed under the CCR rule. Thus, any efforts to develop and apply strategies for groundwater monitoring plans that can be tailored to the specific characteristics of a CCR site, allow updating the site conceptual model, informing choices of remedial alternatives, and adjusting the monitoring program to keep site evaluation and corrective actions on track, will have a significant impact on programmatic costs of groundwater monitoring.



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

Table 1

Table 1 also includes a list of the most frequent constituents that are in assessment or corrective action monitoring programs. The parameters that most frequently exhibit statistically significant increases are lithium (Li), arsenic (As), cobalt (Co), molybdenum (Mo); and to a lesser but still common extent are selenium (Se), barium (Ba), lead (Pb), thallium (Tl), and beryllium (Be). The geochemical behaviors of these constituents are summarized in Table 2. The majority of these constituents exhibit geochemical behaviors that can be quite complex. Factors that promote complexity include sensitivity to pH and oxidation/reduction reactions, the tendency to form dissolved aqueous complexes, and interactions with the solid phase assemblage (i.e., the presence of solubility controls or sorption reactions). Finally, constituents that occur naturally, particularly the minor and trace constituents that have low background concentrations near the detection limit, can be difficult to assess because of spatial variability and limitations to our ability to adequately sample and statistically describe the background population. Our experience has been that constituents that are color-coded green in Table 2 are very likely to benefit from measuring supplemental monitoring parameters, often at a relatively low cost. Supplemental monitoring parameters can help differentiate potential groundwater impacts from a regulated unit from naturally occurring constituents and other sources of impacts to groundwater, and can help keep the regulated unit out of corrective action.



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

🟩 Geochemical Methodologies – OFTEN helpful

🟨 Geochemical Methodologies – SOMETIMES be helpful

🟥 Geochemical Methodologies – RARELY helpful

Table 2

GENERAL INVESTIGATORY METHODS

Regulated units are often sites where construction is or has been occurring for a variety of reasons. In addition, wells often have to be installed into hydrostratigraphic units that are difficult to develop because of fines. Wells may have a low yield, or may not have adequate screen design. Our experience has been that one of the first steps in evaluation, following the occurrence of an apparent SSI above background or apparent SSL above the GPS, is to examine well integrity. Well installation, development, and sampling records should be examined to determine whether suspended solids have been increasing over time and could be the source of a sampling artifact. Well redevelopment is often of great help in reducing total metal concentrations and obtaining samples more representative of aquifer quality. The interior seals and condition of the well casing and screen can be examined via downhole camera to determine whether the well is likely to be compromised, either by physical force (i.e., bent casing or damaged seals) and whether there is a potential short-circuit between shallow groundwater or surface water and the aquifer itself. It should be remembered that low-flow purge methods are not conducive to the long-term stability of monitoring results or obtaining samples that are representative of general aquifer quality in difficult aquifer conditions.

After eliminating sampling artifacts or natural variability as the source of a statistically significant increase, we have found four broad classes of geochemically-based investigative methodologies to be useful in diagnosing groundwater quality issues at CCR-regulated units. The investigative methodologies usually involve measuring supplemental groundwater characteristics (i.e., parameters in addition to the Appendix III and IV lists) to aid in understanding the geochemical characteristics of the system:

- Because of naturally-occurring spatial variability, it is often useful to consider measuring a suite of major anions and cations to classify hydrochemical facies across a site or along a flow path. 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.

- 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 the oxidation state. One technique is to measure oxidation reduction potential (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 concentrations of the different redox species. This information can be used to understand the mobility of dissolved constituents.

- Speciation/solubility/sorption mechanisms also affect fate and transport. These are strongly dependent on pH, the solid phase assemblage that exists along 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.

APPLICATION OF EXTENDED GEOCHEMICAL EVALUATION

EPA 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 need for direct demonstration is applicable whenever the goal is to demonstrate an alternative explanation for the occurrence of Appendix IV parameters at a CCR facility. The following discussion will illustrate how the incorporation of geochemistry beyond the required Appendix III and IV lists can improve the understanding of the potential effects CCR facilities may … or may not … have on the environment.

The first example addresses the issues of relying solely on unfiltered samples collected during routine monitoring. Stabilization of pumping during sample collection typically includes turbidity as measured by a nephelometer (nephelometric turbidity units [NTUs]). Often "stabilization" occurs with 10's of NTUs. As shown on Figure 1, this may represent up to several 100's of milligrams per liter of suspended solids. These solids are not mobile at the flow rates and pore sizes of most aquifers. The suspended solids may include adsorbed elements such as cobalt or cadmium. When samples are acidified as part of standard preservation protocols, the suspended solids may be dissolved or the elements may be desorbed, increasing the apparent aqueous concentrations. This could be critical for elements that have a very low CCR GPS such as cobalt. Given the range of cobalt reported in soil (geometric mean + 2 std. dev of 39 milligrams per kilogram [mg/kg] and maximum of 70 mg/kg, Dragun and Chiasson, 1991), dissolution of 10 to 100 mg/kg of suspended solids could produce on the order of 1 to 10 micrograms per liter (µg/L) in addition to the actual aqueous cobalt concentration resulting in reported concentrations in excess of a 6 µg/L GPS.

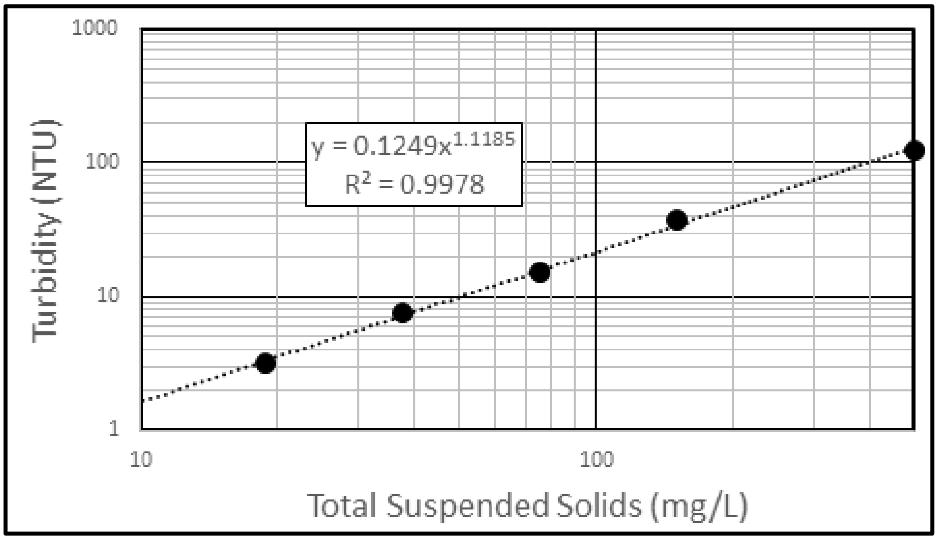


Figure 1. Turbidity as a function of suspended solids content

Cobalt concentrations from a CCR site are shown on Figure 2 where the concentration of total cobalt (dissolved + acidified suspended solids) for several wells exceeds the GPS (background < 0.5 µg/L with turbidity < 1 NTU). There is a clear correlation between the total cobalt concentrations and the concentration of suspended solids in the samples. The sediment contained significant iron concentrations, suggesting that the cobalt may be adsorbing to iron oxyhydroxides. This was confirmed with analyses of aquifer solids as shown on Figure 3. To further demonstrate cobalt adsorption to sediment, laboratory studies found cobalt adsorption to follow a linear adsorption isotherm (Kd of 16.5 to 28.0 L/kg, n=3) up to aqueous concentrations of 120 µg/L. Desorption trials with the sediment found that >95 percent of the cobalt was irreversibly adsorbed when exposed to background groundwater. The use of filtered groundwater and sediment analyses indicated the total cobalt concentrations were an artifact of "stabilized" turbidity produced during sample collection and not necessarily leaching from the CCR facility.

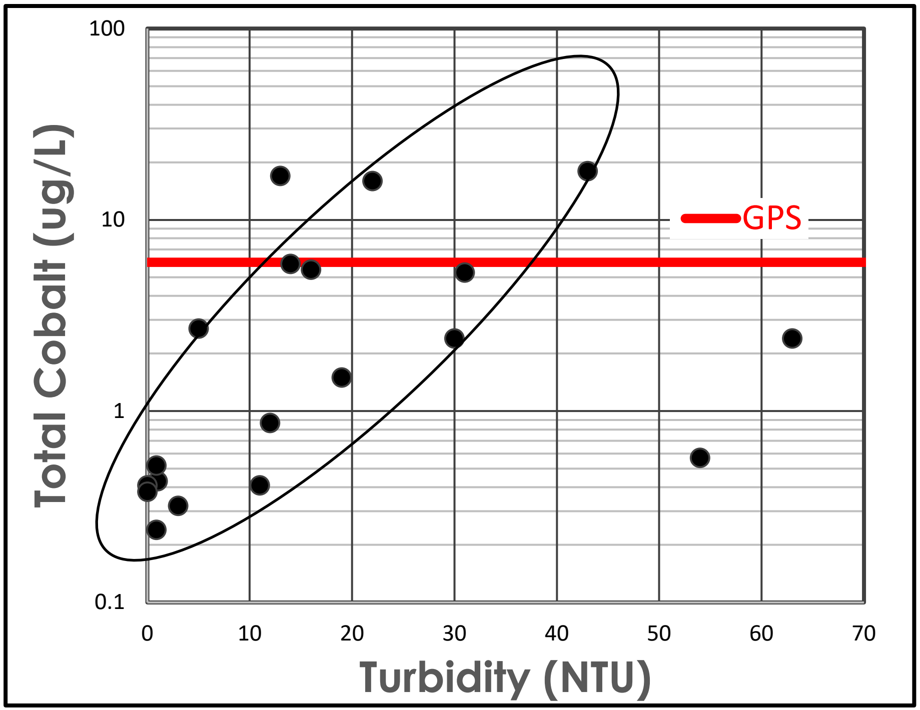


Figure 2. Total cobalt concentrations as a function of turbidity. The cobalt GPS is 6 µg/L.

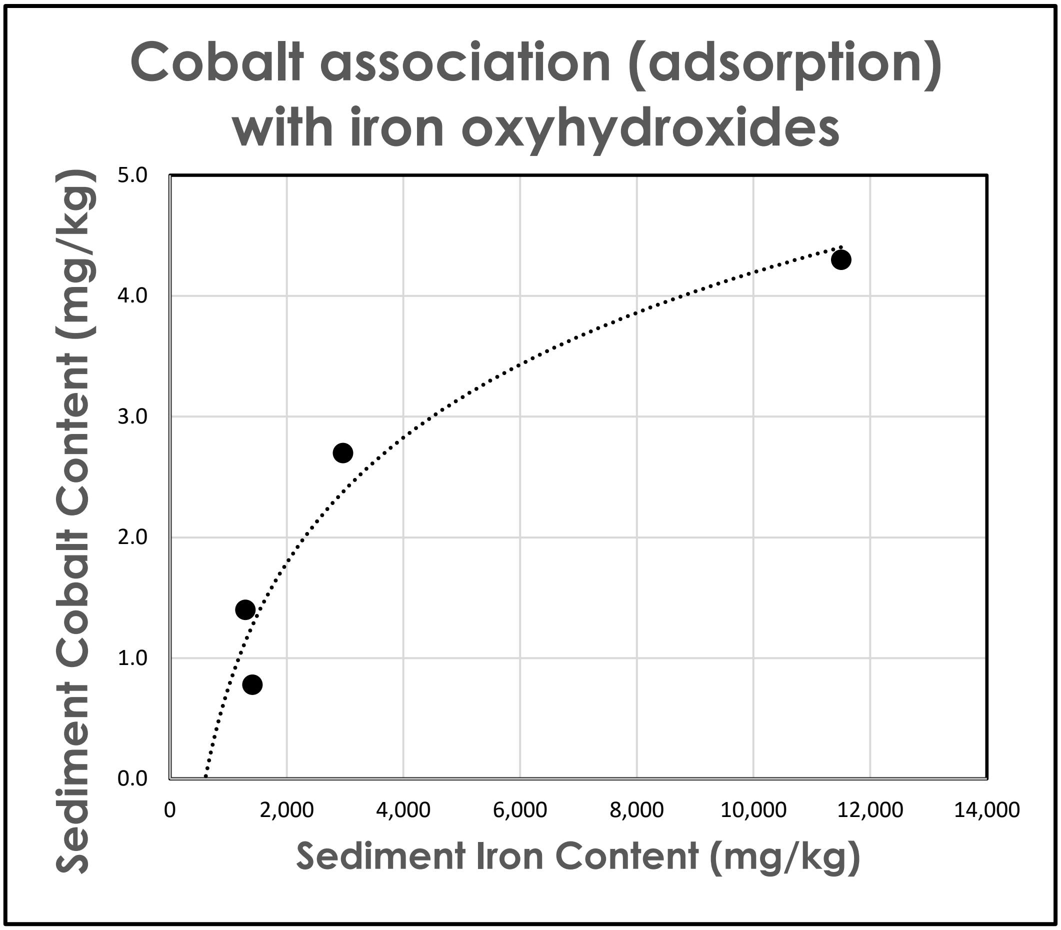


Figure 3. Cobalt association (adsorption) with iron oxyhydroxides.

The second example uses the ORPs measured during sample collection stabilization and iron concentrations to support the conclusion that arsenic observed in a well downgradient does not originate from a regulated CCR unit. Figure 4 illustrates the general hydrogeologic setting and arsenic and ORP observations from this site. Groundwater flows beneath a regulated CCR unit and passes beneath a former pond where CCR residues were removed many years ago and the pond was filled. The background groundwater and deep groundwater from a sandy aquifer not influenced by the regulated unit is oxic (ORP typically 50 to 180 mV) and has low arsenic concentrations (< 1 µg/L). As the groundwater passes beneath the regulated unit the arsenic concentrations increase to as much as 7 µg/L and the ORP to -180 mV. The arsenic concentrations increase to ~60 µg/L only downgradient of the former pond with ORPs typically in the range of -150 to -180 mV. The aquifer material beneath and downgradient of the former pond is black, organic-rich, silt and sand fill that appears to have been used to construct the former pond. These observations suggest that the low ORP may be driving the release of arsenic from the fill materials, possibly as a result of the dissolution of iron oxyhydroxides that have absorbed arsenic (Stollenwerk, 2003). The results of iron analyses added to the routine monitoring program are shown on Figure 5. The samples with high arsenic concentrations downgradient of the former pond are co-located with high iron concentrations and low ORP; supporting the proposed source of arsenic as a result of iron oxyhydroxide dissolution. To further support this process, future testing can confirm the sediment as a source of the arsenic to complete the demonstration of an alternate source.

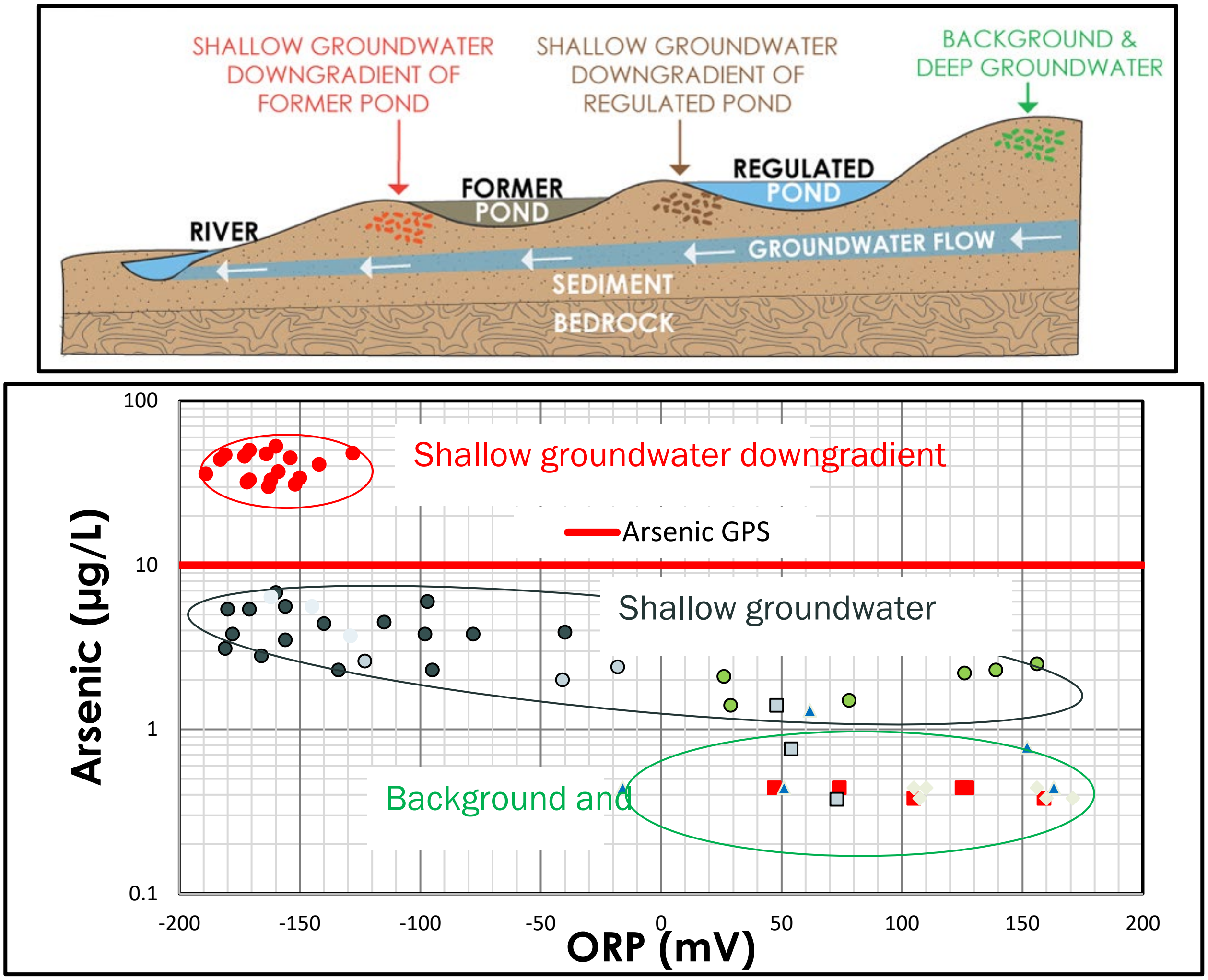


Figure 4. Hydrogeologic setting and arsenic occurrence.

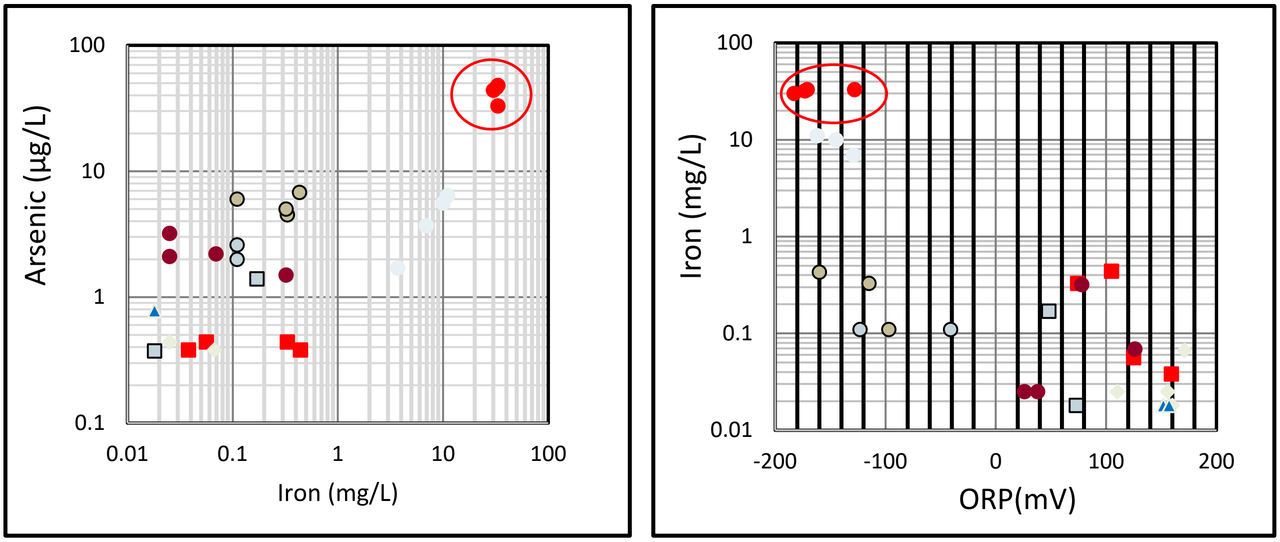


Figure 5. The relationships between arsenic, iron and ORP.

CONCLUSIONS AND RECOMMENDATIONS

A nationwide snapshot of corrective actions finds that common Appendix IV constituents of potential concern (COPCs) include arsenic, cobalt, lithium, and molybdenum. Site testing may need to address constituents in addition to Appendix III and IV to adequately evaluate the need for and scope of Corrective Actions because the origin, fate, and transport of Appendix IV constituents may be controlled by mineral precipitation/dissolution, complexation, and/or adsorption. Factors controlling these processes include pH, ORP, valence state, counter ions, suspended solids, and matrix solids. Of the common COPCs, arsenic and cobalt are most influenced by these processes.

Demonstrating an understanding of the underlying processes is instrumental to successful arguments for monitored natural attenuation or alternate sources. Such demonstrations may require the use of some or all of the following: field measurements (e.g. pH, ORP, or turbidity), major and minor cations and anions, additional trace elements (e.g. iron), and the evaluation of aquifer solids.

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