Alternative Source Demonstrations: 
Sleuthing in the CCR Program

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1. Abstract
The use of Alternative Source Demonstration (ASD) at a coal combustion residual (CCR) Unit requires the right tools, experience, approach and investigative savvy. The result of an ASD determination has significant implications to the planning and expenditures of funds associated with CCR Rule compliance. This presentation will review and evaluate the what, when, why and how behind the use and implementation of an ASD.

The What:
- An ASD is a regulatory acceptable option available to demonstrate that the CCR Unit may not be the source of groundwater protection standards (GPS) concentration exceedances.

The When:
- The time to complete the ASD is after a sampling event with a statistically significant increase (SSI) above GPS.

The Why:
- Contaminants from an alternate source can be better addressed under a more flexible regulatory program potentially allowing for significant cost savings.

The How:
- Determine if the Unit monitoring well network is accurately located to detect GPS exceedances from the CCR unit only.
  - Is there a separate off-site source; or
  - On-Site source such as a leachate collection pond/sedimentation basin?
- Determine if the analytical method is correct and accurate enough to detect a SSI.
- Review groundwater geochemical conditions (commonly used ‘Geochemical Forensic Tools’) that may have changed.
- Confirm the sample collection methodology was conducted in accordance with the groundwater monitoring plan (GWMP).
  - Were flowrates and turbidity levels sufficiently low?
  - Were stability parameters satisfactory prior to sample collection?
  - Other appropriate considerations
The presentation will build on our experiences with successful CCR ASD demonstrations.

2. **The What**

A critical part of the CCR Rule is the requirement for groundwater monitoring and subsequent corrective action implementation should a release to the environment be discovered. The Rule requires the following steps at new and existing CCR units:

- Installation of a groundwater monitoring network
- Implementation of a Detection Monitoring Program (DMP) that establishes the following:
  - Background concentrations for Appendix III and IV (in Title 40 of the Code of Federal Regulations (CFR) part 257) compounds
  - Semiannual sampling of Appendix III compounds

The Appendix III analytical results are required to be statistically evaluated, and if a statistically significant increase (SSI) is identified greater than the established background concentrations, the initiation of an Assessment Monitoring Program (AMP) is required.

Once triggered, an AMP consists of sampling wells for Appendix IV parameters and comparison to groundwater protection standards (GPS), which is the United States Environmental Protection Agency (EPA) Maximum Contaminant Level (MCL); alternative groundwater protection standards listed in 40 CFR 257.95(h)(2); or established background concentration. If one or more of the constituents exceeds the GPS, then Corrective Action must be initiated.

In specific instances when the detected constituent is considered to be from a source other than the CCR unit, the Rule also allows for an ASD. As outlined in 40 CFR 257.95(g)(3)(ii), owners or operators of CCR units may complete the following:

> Demonstrate that a source other than the CCR unit caused the contamination, or that the statistically significant increase resulted from error in sampling, analysis, statistical evaluation, or natural variation in groundwater quality. Any such demonstration must be supported by a report that includes the factual or evidentiary basis for any conclusions and must be certified to be accurate by a qualified professional engineer.

Thus, ASDs are an important regulatory acceptable option available for use in demonstrating that the CCR unit may not be the source of GPS exceedance.
3. The When
An evaluation of the potential for alternate sources is triggered after a sampling event with a SSI above GPS. However, the ideal time to understand potential alternate sources is before, during, and immediately after sampling. Having a comprehensive understanding of the groundwater monitoring system could also help prevent the potential for SSI occurrences.

A selection of items that should be evaluated are presented below:

Well Location
- Is the well network located to detect groundwater at the disposal unit boundary (DUB), or are there other potential sources such as leachate collection ponds or sedimentation basins?
- Are there wells in swampy areas or under water due to run-on from off-site?
- Are the wells screened in the correct aquifer?
- Do the subsurface conditions or geology change dramatically from upgradient to downgradient wells?

Alternate Sources
- Are there other potential sources in the area that could reasonably influence groundwater constituent concentrations?
- Are there historical practices in the area that may have contributed metals to the groundwater?

Sampling and Analysis
- At the conclusion of groundwater sampling:
  - Were the field parameters during sample collection in range?
  - Was the turbidity acceptable?
  - Was there a change in the physical well?
  - Were any changes noted in the area?
- Is the correct analytical method being used with acceptable detection limits?

4. The Why
False positive SSIs can lead to additional work and result in corrective actions that are a result of errors in well placement, alternate sources, or sampling/analysis and not actual releases from CCR units.

If it is demonstrated that the source of the contamination, through a successful ASD, is a source other than the CCR unit itself, additional options become available to address the issue. Significant cost savings can be realized through addressing corrective actions under a more flexible regulatory program and the potential use of risk assessments not offered under the CCR Rule.
5. The How
There are multiple potential causes of SSIs that are not associated with releases from the CCR unit. This paper outlines a selection of the potential issues.

5.1 Monitoring Well Network
The Rule is specific about the purpose of the groundwater monitoring well network. As outlined in the Federal Register (80 FR 21399),

“All groundwater monitoring systems must consist of a sufficient number of appropriately located wells (at least one upgradient and three downgradient wells) in order to yield groundwater samples from the uppermost aquifer that represent the quality of background groundwater and the quality of groundwater passing the waste boundary.”

The waste boundary is defined in 40 CFR 257.53 as “a vertical surface located at the hydraulically downgradient limit of the CCR unit”.

Clarification regarding leachate basin applicability to the CCR Rule was provided in the Frequent Questions on the Implementation of the Disposal of Coal Combustion Residuals (CCR) from Electric Utilities Final Rule (USEPA – November 2, 2017) which addresses the question of, “Are coal ash leachate ponds subject to this rule?”

“RESPONSE: No. The rule regulates CCR landfills and CCR surface impoundments. CCR surface impoundments are defined as impoundments that are designed to hold an accumulation of CCR and liquids, and that treat, store, or dispose of CCR. A CCR leachate pond, or impoundment; i.e., an impoundment that only holds leachate from CCR landfills and not CCR, does not meet this definition.”

Therefore, as outlined in the Rule and guidance, a well that is downgradient of a leachate pond or sediment basin is not considered representative of the waste in the CCR unit, and any detection of elevated constituents in the well would not be subject to the CCR Rule.
Other potential on-site sources of CCR constituents that are not subject to the CCR Rule would be CCR that is placed on the land prior to being beneficially used off-site, or uniquely associated wastes such as equipment (boiler, precipitator, etc.) washes.

In addition to on-site sources, there may be off-site sources of CCR constituents. For example, boron is found as an active ingredient in herbicides, pesticides, and fertilizer as well as many other products.

5.2 Analytical Method
Each analytical method has limitations on the accuracy of the instrument and level of detection. This is particularly true of field measurements such as pH. Each instrument has an inherent error that can be up to ±0.2 standard units. There can also be issues with calibration fluids and a calibration drift as the instrument is used during the day.

In addition to field parameters, analysis conducted by off-site laboratories need to be evaluated. Deliberate consideration must be given to the analytical method chosen for CCR constituent analysis (e.g., ICP vs ICP/MS). The use of inconsistent analytical method may result in inaccurate data sets that are not directly comparable from event to event. This is especially true when the detection limit varies and statistical analysis are involved.

5.3 Groundwater Sample Collection
As outlined in the Federal Register (80 FR 21397), EPA requires “consistent sampling and analysis procedures.”
It is of the upmost importance to understand the geochemistry of the subsurface. Changes in geochemistry can result in changes in the concentration of constituents. For every sample that is collected, the following corresponding field parameters need to be collected and evaluated for a change from previous sampling events:

- pH
- Temperature
- Dissolved Oxygen
- Oxidation-Reduction Potential (ORP)
- Turbidity

These parameters need to be evaluated to determine if the change in concentrations of one or more constituents are due to the changes in geochemical conditions at the site. A complete understanding of the geochemical conditions is critical, as samples collected outside of the prescribed parameters may result in a false positive result. For example, samples collected with elevated turbidity levels may result in an elevated concentration of metals that have adsorbed to suspended solids in the same and not indicative of concentrations dissolved in groundwater.

Variable turbidity level in samples can greatly affect detected concentrations

### 5.4 Geochemical Forensic Tools

A successful ASD depends not only on a good understanding of site conditions, but also on effective communication of the subsurface processes. An effective ASD approach will include the evaluation of geochemical site conditions and comparison of constituent distribution at a site to that of known sources as well as to the area surrounding the site. The choice of which geochemical evaluation (forensic) tool(s) to use during an individual ASD is site-specific, as each site has different needs. The following section presents some of the most useful geochemical forensic tools for ASDs at CCR facilities.

#### 5.4.1 Geochemical Ratio Analysis

While the chemical composition of the leachate from a CCR impoundment can vary from site to site, or even over time, there are several parameters that are commonly
found at most sites. By examining the relative proportions of the parameters in the groundwater samples collected, a characteristic signature (fingerprint) of the CCR at a site can often be determined. The parameters included in such a fingerprint analysis should not be limited to heavy metals alone, but should also include minor ions such as boron, and major ions such as calcium, chloride, and sulfate.

There are several ways to evaluate these fingerprints during an ASD; the most straightforward is to identify the key parameters within the well exhibiting the GPS exceedance and the known CCR leachate. If it can be demonstrated that the ratio(s) of the key parameters at the GPS-exceeding well and the CCR leachate are different, then this is powerful evidence in support of an ASD.

The communication of the results of the ratio method can sometimes be difficult to communicate if there are multiple parameters involved. In cases where multiple parameters are important for the evaluation of the fingerprint, multi-axis radial diagrams can often be an effective evaluation and communication tool. Radial diagrams allow the simultaneous plotting of the concentrations of multiple parameters on a single diagram. Each axis radiates away from a central point, and the concentrations plotted on each axis are then joined and the internal area is shaded. The overall shape of the shaded area is then compared to the shapes at other wells.

**Radial Example.** Shape of the chemistry at the sump location is distinct from several of the samples collected to the east and south, suggesting that multiple sources are present.

EPA developed a protocol for evaluating leachate sources that they called the Fingerprint Analysis of Leachate Contaminants (FALCON) (USEPA, 2004). The FALCON procedure includes comparing the normalized concentrations between two locations using linear regression, and then comparing the “goodness of fit” results ($r^2$ values) of the linear regression line to determine the similarities between the samples.
Plotting the $r^2$ values on a map is a useful way to track the relationships between samples collected in different areas to determine if there is a site-wide pattern.

The choice of which parameters to include for the radial diagrams or FALCON procedure is site-specific, but using parameters that are resistant to degradation and precipitation result in a more reliable fingerprint.

### 5.4.2 Isotopes

For coal ash impoundments, isotopic analysis of some of the major constituents can help determine their origin. For example, in areas where the natural sulfate concentration in groundwater is very high, sulfate concentrations in monitoring wells alone cannot be used as an indicator of impact from a coal ash impoundment. However, the isotopic ratio of sulfur in the sulfate can provide evidence of coal ash-derived impacts. Zielinski et al. (2005) describe a study where the isotopic ratio of sulfur in sulfate collected from groundwater downgradient of a coal ash impoundment was shown to be distinct from the local background sulfur ratio and similar to the ratio of sulfur found in sulfate from coal ash.

The isotopic signature of boron from coal ash is distinctive from naturally occurring boron, or boron from other anthropogenic sources (Ruhl, et al., 2014). Most importantly, the use of isotopic tracers can allow coal ash contamination to be distinguished from other similar contamination coming from different sources in a catchment, while also linking other constituents associated with coal ash back to the source.

The isotopic ratios of carbon, hydrogen, and oxygen, among others, can be used in a similar way to help determine the source of groundwater constituents and of the water itself. It should be noted, however, that isotopes should not be used without a strong understanding of the local hydrogeology and geochemistry, and an isotopic evaluation should only be undertaken as part of a broader sampling program.

### 6. Summary

In summary, there are multiple considerations that require evaluation when performing an ASD for SSIs in groundwater; and the ASD evaluations should be conducted at the commencement of the sampling program and continuously reevaluated throughout the monitoring program.

There is no one size fits all method for conducting ASGDs. An ASD is a comprehensive evaluation including a unit by unit assessment of potential sources, geochemical variation in groundwater, sampling and analysis techniques, and statistical evaluation of the data.
References

