An Approach to Using Geochemical Analysis to Evaluate the Potential Presence of Coal Ash Constituents in Drinking Water

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ABSTRACT

A geochemical evaluation approach was developed to compare water quality data collected from monitoring wells located within, upgradient, and downgradient of a hypothetical coal ash pond system to determine the degree to which local water supply wells were affected by ash pond constituents. The data set for the system was generated based on general water quality characteristics found in vicinity of a typical ash pond system, which was comprised of water samples collected from: ash pond monitor wells, monitor wells screened in the saturated zone below the ash ponds; monitor wells located upgradient and downgradient of the ash ponds; and nearby water supply wells. Use of a series of geochemical plots allowed for identification of indicator compounds tied to the oxidation reduction state of the sampled water and to common coal combustion residual (CCR) indicator constituents such as sulfate and boron. A parallel statistical analysis was performed to determine background threshold values (BTVs) for CCR constituents using site-specific and regional data. A comparison between the BTVs for each compound and the water supply well data was performed to determine whether water supply wells contained naturally occurring levels of inorganics or whether the detected inorganics were CCR-derived and due to migration from the ash pond systems. The results indicate that the approach can provide strong evidence to help determine whether off-site water supply wells are or not impacted by CCR releases to groundwater.

INTRODUCTION

Several constituents present in coal ash can serve as indicators of a release from a coal ash management area to groundwater. These constituents have been used by U.S. Environmental Protection Agency (USEPA) to design the groundwater monitoring program under the final CCR Rule[1]. Detection monitoring is required for the following list of "indicator" constituents identified in Appendix III of the CCR Rule: boron, calcium, chloride, fluoride, sulfate, and total dissolved solids (TDS). These constituents are generally soluble in water, and potentially useful as CCR impact indicators. Of these, boron and sulfate are the most common constituents used to evaluate the extent of CCR-impacted groundwater. However, because these constituents are also naturally occurring, their presence at concentrations higher than water quality objectives/goals may simply reflect the background groundwater conditions. Therefore, multiple lines of evidence are required to help assess a potential CCR impact to groundwater in nearby local water supply wells.

A site-specific groundwater flow model is a useful tool to describe the groundwater flow field under the present hydrogeologic conditions. Groundwater flow modeling can provide insights for ash basin management and help assess whether extracted groundwater from any local water supply well may be affected by CCR-impacted groundwater. Nevertheless, because of uncertainty associated with past hydrogeologic conditions, pumping history, and nearby local water supply well construction, additional lines of evidence can be used to corroborate groundwater flow modeling results to reduce modeling uncertainty.

Other lines of evidence can be provided by comparing the geochemistry of ash basin porewater, impacted and non-impacted groundwater within a CCR facility, groundwater in local water supply wells, and groundwater in regional background wells, as well as wells in similar hydrogeochemical conditions. Because collected groundwater concentration data represent combined historical influence of the past ash basin management and pumping of local water supply wells, an in-depth geochemical analysis is expected to provide results that consider a changing hydrogeologic environment. The following describes the approach and methodologies used for a comparative geochemical evaluation.

GEOCHEMICAL EVALUATION APPROACH AND METHODS

The overall objective of the geochemical evaluation in support of groundwater flow modeling is to assess whether the CCR-impacted groundwater at a CCR site may have resulted in water quality exceedances found in nearby local water supply wells. The multi-step evaluation approach consists of the following key steps:

Step 1. Screen the biogeochemical and transport behaviors of key CCR-related constituents under site specific aquifer conditions to establish candidate constituents for further evaluation;

Step 2. Assess the presence and magnitude of typical CCR candidate constituents in the groundwater beneath a CCR site (due to ash basin system releases) and the outside of the site. Site monitoring wells and offsite water supply wells may be grouped according to their purpose of monitoring, well types, and distance to the ash basin system. The following simple well grouping has been found useful: (1) ash basin porewater monitoring wells, (2) other facility monitoring wells, (3) nearby local water supply wells, and (4) regional background wells.

The purpose of this data grouping is to obtain a quick assessment of the spatial concentration trend in relationship to distances to the source of CCR-impacted groundwater (i.e., ash basin porewater). Note that wells in a group may be further divided into subgroups to refine the evaluation of spatial concentration trends. The boxplot method is a useful tool for this assessment;

Step 3. Identify useful redox constituents that can also serve as an indicator or a signature for CCR-impacted groundwater by comparing the concentration magnitude of dissolved oxygen, iron, and manganese, among various well groups;

Step 4. Select the most promising constituents that can differentiate the site-related impacts and background conditions to serve as signature constituents to assess the potential relationship between the facility CCR-impacted groundwater and the local water supply wells. Use two-dimensional correlation plots to reveal the data clustering pattern for a pair of signature constituents according to various well groups. The pattern may help identify local water supply wells that are potentially affected by CCR-impacted groundwater;

Step 5. Compare the relative abundance patterns of major cations and anions in groundwater among various well groups to assess the data clustering pattern among various well groups. Piper plot is a useful diagnostic tool for this assessment;

Step 6. Establish the background threshold values (BTVs) for the selected signature constituents via concentrations in CCR facility background wells, nearby water supply wells, regional background wells, and literature data for the aquifer system of interest with site-specific considerations about what data can be considered to represent the background conditions. The BTVs can be estimated using the ProUCL software[2]; and

Step 7. For the local supply wells that show a sign of potentially being affected by impacted groundwater, as identified through the evaluation approach above, an evaluation of the spatial distribution of potentially impacted wells and non-impacted wells together with the results of groundwater flow modeling and relevant well information (e.g., construction, depth, and pumping rates) to reduce the possibility of false-positive identification of potential impacted local water supply wells.

The following provides the description of the tools that can facilitate the evaluation.

<u>Box plot:</u> The comparisons of the concentration magnitude among different well groups for various potential indicators can be made using box plots produced by the ProUCL software[2]. Figure 1 defines the various components of a box plot. The location of the upper whisker is the lesser of 1.5 times the interquartile range (IQR) above the 75 percentile or the maximum value; the location of the lower whisker is the greater of

1.5 times the IQR below the 25 percentile or the minimum value. This analysis can include both detected values and non-detects (NDs).

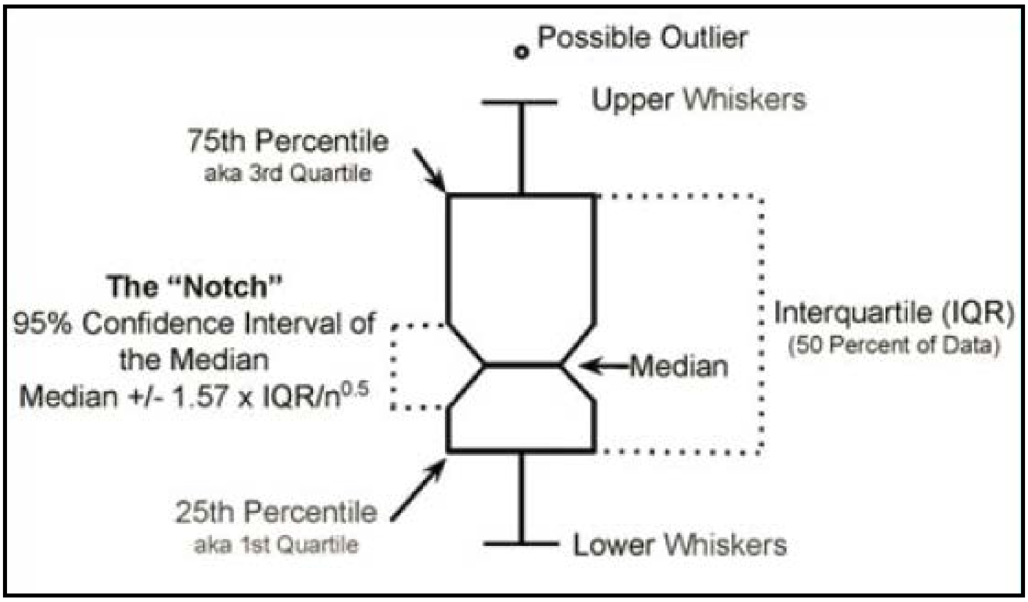
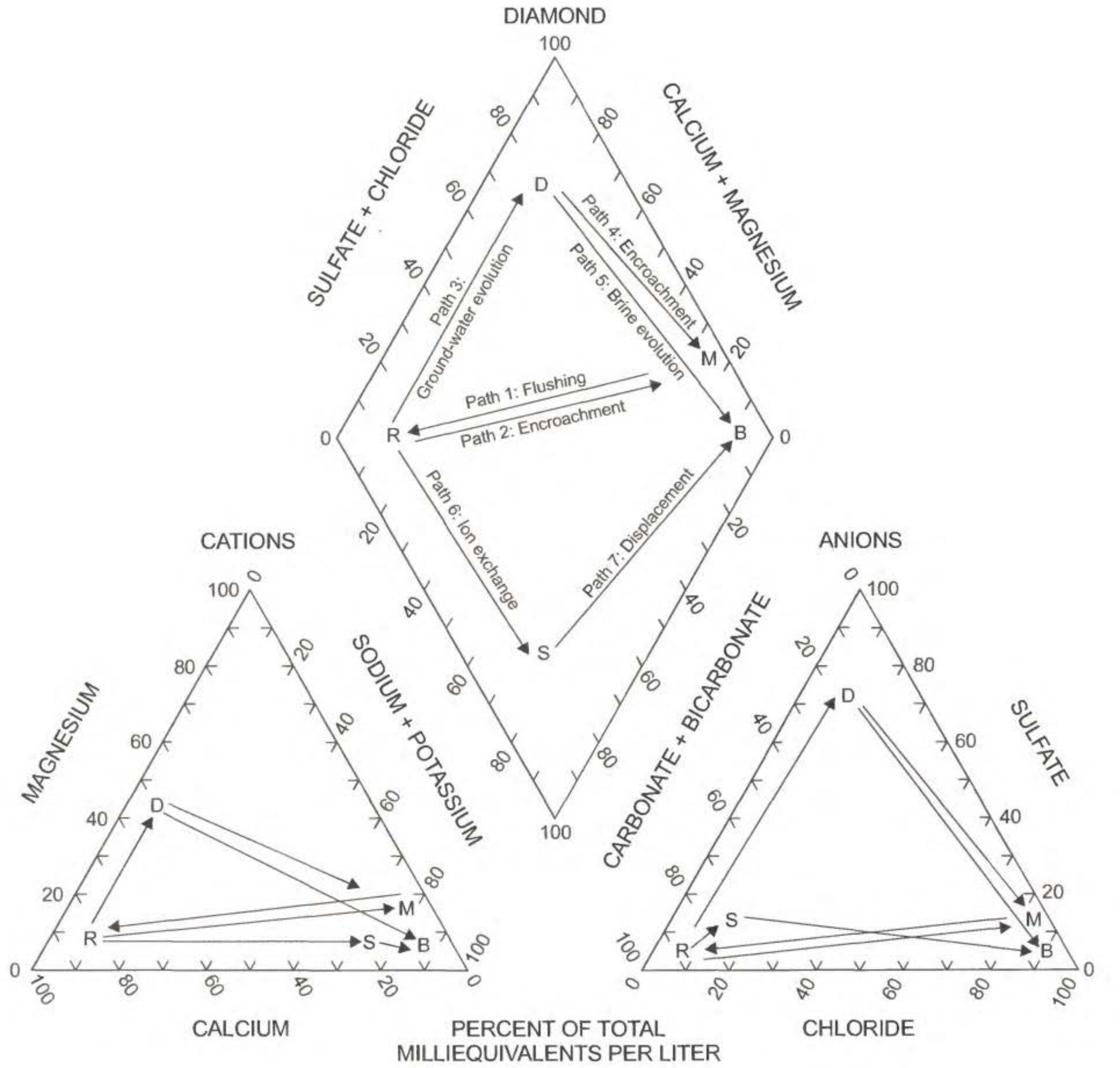


Figure 1: Example box plot (adopted from https://sites.google.com/site/davidsstatistics/home/notched-box-plots)

Correlation Plot: The data associated with identified signature constituents can be used to generate correlation plots to further evaluate the relationships among various data groups. To create a correlation plot, different data groups can be plotted using different symbols with the concentrations of one constituent on the x-axis and the concentrations of the other constituent on the y-axis. The clustering patterns or trends will illustrate the correlations among data groups.

Piper Plot: Piper plots have been frequently used to assess the relative abundance of general cations (sodium, potassium, magnesium, and calcium) and anions (chloride, sulfate, bicarbonate, and carbonate) in groundwater and to differentiate different water sources in hydrogeology[3]. Groundwater resulting from different water sources or in different geologic units may exhibit distinct clustering patterns on a Piper plot. Because calcium, sulfate, and chloride are common coal ash constituents, it is expected the CCR impacted groundwater may show a different clustering pattern than the background groundwater or the groundwater that has not been impacted by CCR. The data clustering pattern may also reveal possible mechanisms of major ion composition shift due to natural geochemical reaction processes. Figure 2 provides an example of the Piper plot and some geochemical reaction mechanisms that may result in a shift of major ion composition in groundwater[4].



EXPLANATION

CHEMICAL COMPOSITION	REACTION PATHS	DOMINANT PROCESS
M MARINE WATER	PATH 1 M → R	Recrystalization of aragonite to calcite. Selective dissolution of aragonite. Inversion of calcite from high-magnesium to low-magnesium. Cementation
R RECHARGE WATER	PATH 2 R → M	Simple mixing. Dissolution in dispersion zone
S SOFT WATER	PATH 3 R → D	Dissolution of dolomite and gypsum. Dedolomitization
D DOWNGRADIENT WATER	PATH 4 D → M	Dolomitization
B BRINE	PATH 5 D → B	Dissolution of halite
	PATH 6 R → S	Ion exchange on clay sediments. Replacement of calcium and magnesium ions by sodium ions
	PATH 7 S → B	Displacement of soft water by mineralized water within a confined aquifer

Figure 2: Reaction paths for evolution of major ion composition of groundwater in a Piper plot[4].

HYPOTHETICAL SCENARIO

To illustrate the use of the geochemical evaluation approach described above, a hypothetical hydrogeologic setting was assumed. The conceptual site model for the hypothetical scenario is illustrated in Figure 3.

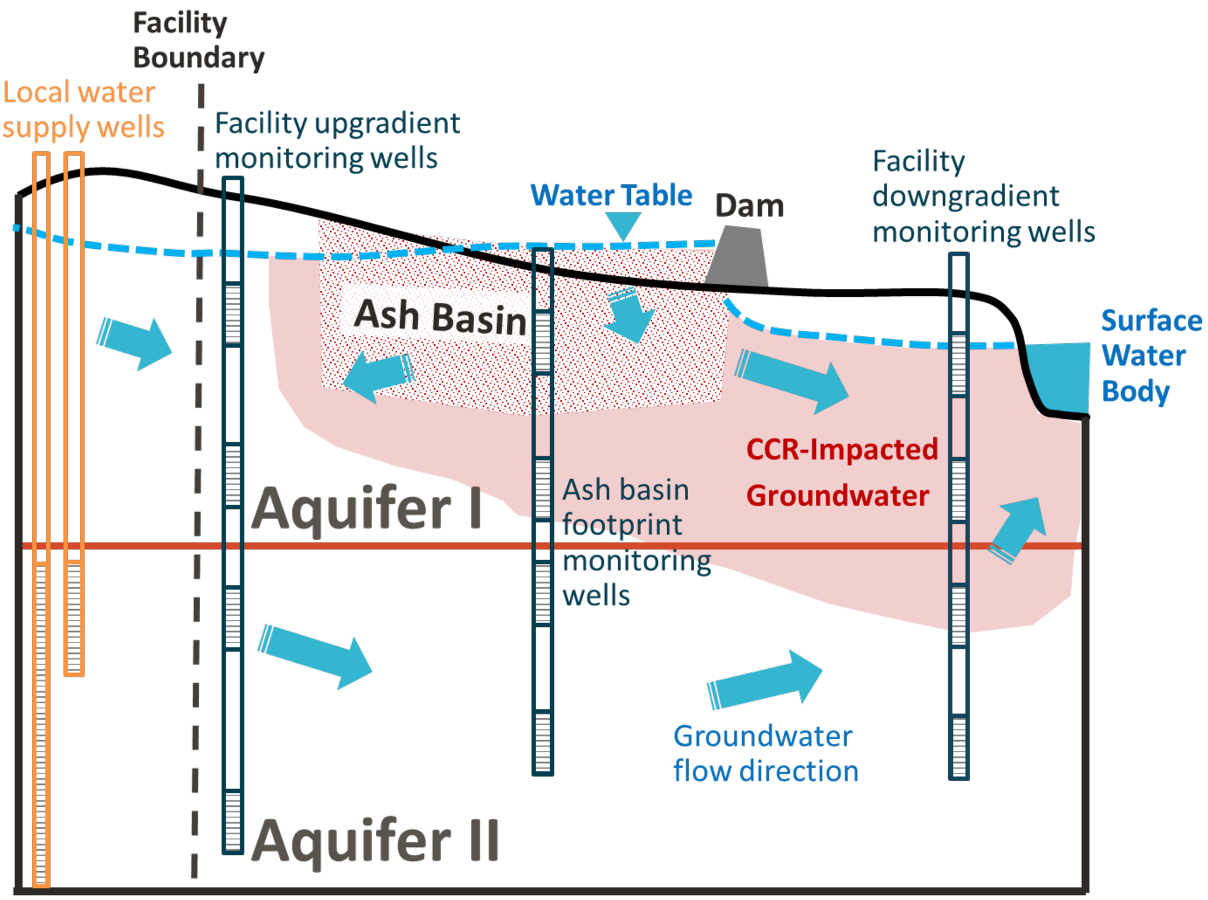


Figure 3: Schematic of the conceptual site model for the hypothetical scenario

Many CCR sites possess hydrogeological settings like the features shown in Figure 3; these features are:

- CCR facilities are often close to a surface water body;
- Groundwater impacted with relatively high concentrations of CCR constituents is generally found in the shallow unconfined surficial aquifer unit (Aquifer I). Groundwater in the deeper aquifer units often suffers less impacts;
- Ash basin management practices often result in a downward hydraulic gradient and localized groundwater flow field different from the general regional flow direction in the vicinity of the ash basin;

- Local water supply wells are generally at perceived upgradient or side gradient locations in terms of the general regional groundwater flow direction and the ash basin location or at locations across a surface water body (e.g., rivers or lakes); and

- Local water supply wells often have different well depths and often obtain groundwater from the deeper aquifer units and not directly from the surficial aquifer.

EVALUATION DEMONSTRATION

To facilitate the demonstration of the geochemical evaluation process, the data set from an unnamed site is used here. The following presents how the evaluation steps described in the previous section and site-specific information applied to the data set.

<u>Step 1 – Initial screening for signature constituents</u>: Besides boron, calcium, chloride, sulfate, and TDS (major CCR constituents in Appendix III of the CCR rules), site-specific sorption experiments indicate that barium and cobalt are less sensitive to the redox conditions and not readily sorbed to mineral surface under site-specific geochemical conditions, and thus are considered candidates for signature constituents.

<u>Step 2 – Box plot comparison of the candidate signature constituents</u>: The concentration magnitude of the candidate constituents among various well groups are compared using the box plot method. The well groups consist of ash basin porewater monitoring wells, facility monitoring wells, nearby local water supply wells, and regional background wells. The most promising signature constituents are those that can provide large concentration contrast between concentration found in ash basin porewater and nearby local water supply and regional background wells. The results are shown in Figure 4.

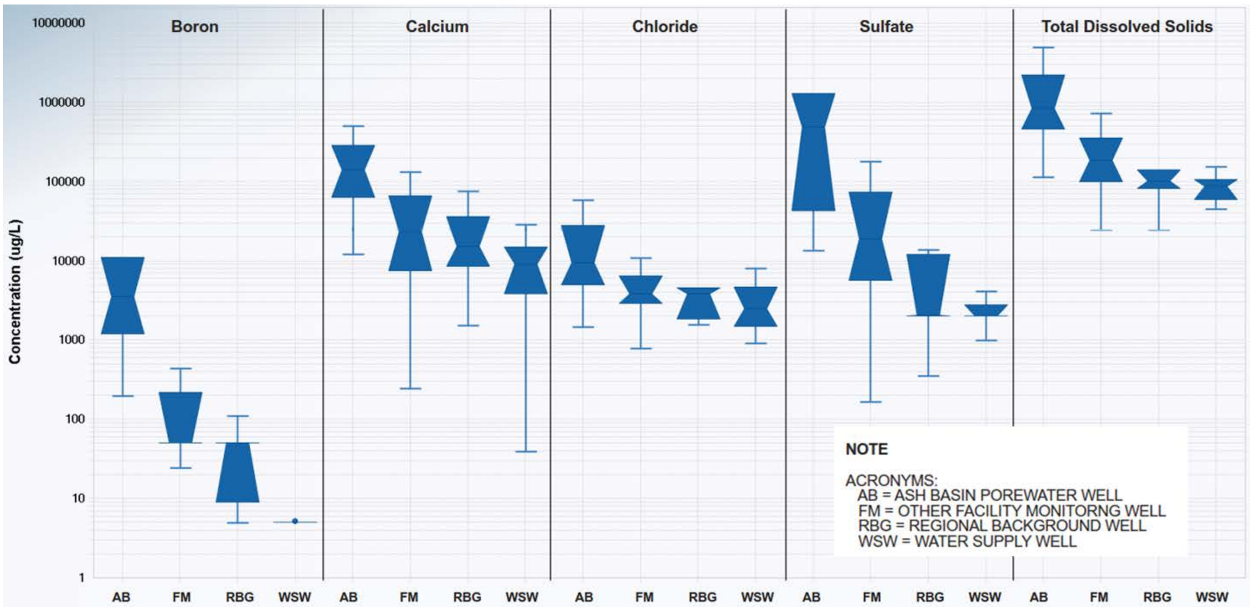


Figure 4: Concentration magnitude comparison of five CCR indicators.

Based on the box plot comparison (the results of barium and cobalt are not shown), the most promising signature constituents are boron and sulfate because these two constituents provide the most significant contrast among different well groups, indicating that the extent of CCR-impacted groundwater can be delineated better because site-specific background concentrations for boron and sulfate are less likely to significantly mask the impacts of ash basin leachate to groundwater.

<u>Step 3 – Box plot assessment of redox candidate constituents</u>: Dissolved oxygen, dissolved/total iron, and dissolved/total manganese are three useful redox constituents to indicate anoxic or anaerobic conditions. The results of the box plot comparison for these constituents are shown in Figure 5.

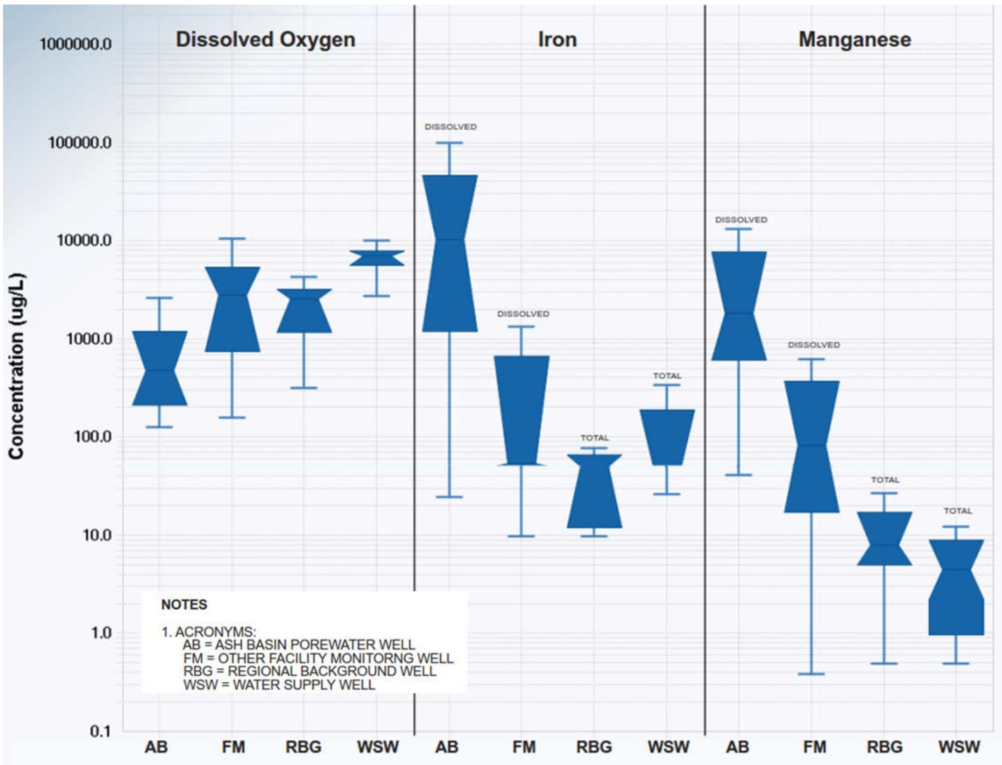


Figure 5: Concentration magnitude comparison of three redox indicators.

The trend of dissolved oxygen concentrations shows that the groundwater in the nearby local water supply wells is generally significantly more oxygenic than the porewater in the ash basin porewater. The observed low oxygen concentrations in the ash basin porewater are consistent with the understanding that coal ash leachate is a chemically reduced solution[5]. The depletion of dissolved oxygen in the leachate is attributed to the occurrence of sulfite or other oxidation processes when oxygenic water contacts with coal ash[5]. The iron and manganese concentration trends are opposite to that of dissolved oxygen. The results are consistent with the iron and manganese geochemical behavior in that they tend to form precipitates under oxygenic conditions, thereby being removed from the groundwater.

Under the hydrogeologic conditions at the unnamed site, dissolved oxygen occurs in groundwater through recharge by precipitation and air within the unsaturated zone. Dissolved oxygen remains in groundwater until it is used by bacteria, organic material, or reduced minerals[6]. High dissolved oxygen concentrations in groundwater may indicate relatively rapid groundwater recharge[6]. Since low dissolved oxygen concentrations are expected to occur downgradient of the ash basin(s), the lack of dissolved oxygen is considered as an effective signature. If the groundwater obtained by a local water supply well is primarily from the ash basin, it is expected that the dissolved oxygen concentration would be low because there is no effective mass transfer process to increase the dissolved oxygen concentration during groundwater transport in the deeper aquifer (see Aquifer II in Figure 4). In contrast, although high dissolved iron and dissolved manganese can also indicate anoxic groundwater conditions, these constituents tend to be re-oxidized and form precipitates when they migrate into an aquifer system containing mineral oxides. Therefore, dissolved iron and dissolved manganese are less indicative of the presence of CCR-impacted groundwater than dissolved oxygen. Based on this assessment, dissolved oxygen is selected to be a signature constituent.

<u>Step 4 – Two-dimensional correlation plots of signature constituents</u>: Display of the signature constituents, boron, sulfate, and dissolved oxygen, can further help explore the nature of the concentration distributions. Aquifer II is the water source for the local water supply wells (Figure 3). In the correlation plot evaluation, the data for boron, sulfate, and dissolved oxygen are grouped as follows: (1) ash basin porewater wells, (2) water supply wells, (3) regional background wells, and (4) CCR facility monitoring wells screened in Aquifer II, which are further divided into three subgroups – upgradient wells, side gradient wells, and downgradient wells. The definitions of upgradient, side gradient, and downgradient are based on the interpretation of recent groundwater flow directions using site-specific water elevation data and the groundwater flow modeling results. The correlation plots for the pair of boron and sulfate and the pair of boron and oxygen are shown in Figure 6 and Figure 7.

The data pairs for the facility Aquifer II wells that are classified as the downgradient group (which are most likely to exhibit the impact of ash basin leachate to groundwater), are generally clustered toward the ash basin porewater data pairs (Area 1). In contrast, the data pairs of the side gradient and upgradient wells are generally clustered toward the local water supply and regional background wells (Area 2). Figure 6 shows that the facility downgradient bedrock wells are either in Area 1 or exhibit a significantly higher sulfate concentration than those of the nearby water supply wells. All upgradient and side gradient bedrock wells, except MW-1, show similar lower boron and sulfate concentrations to those observed in the local water supply wells. Figure 7 shows that the low oxygen and elevated boron concentrations serve as an effective signature pair to help identify the CCR-impacted groundwater. The fact that most of the water supply wells are significantly more oxygenic demonstrates that the water supply wells do not obtain groundwater primarily from the ash basin system. Because the locations of the regional background wells are very far from a CCR facility, the observed concentrations are considered to reflect non-CCR-impacted groundwater conditions. It is noted that the concentrations observed in these regional background wells show significant concentration variability. The large concentration variability observed among the regional wells strongly suggest that it is not possible to establish a simple concentration threshold to ambiguously indicate CCR impact.

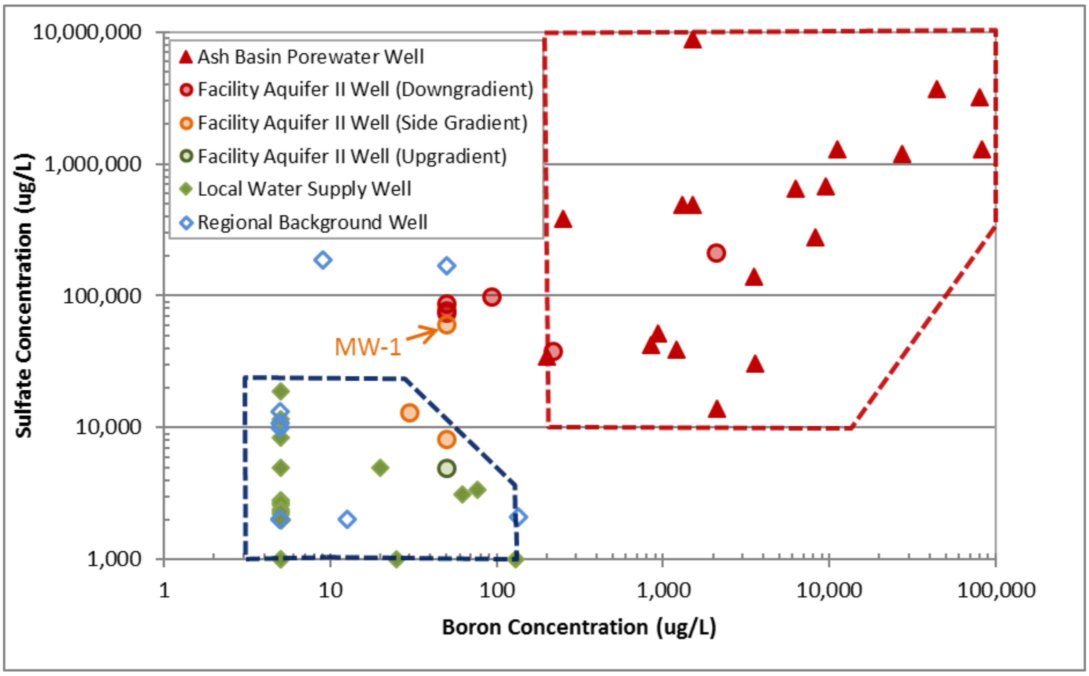


Figure 6: Correlation plot for boron and sulfate.

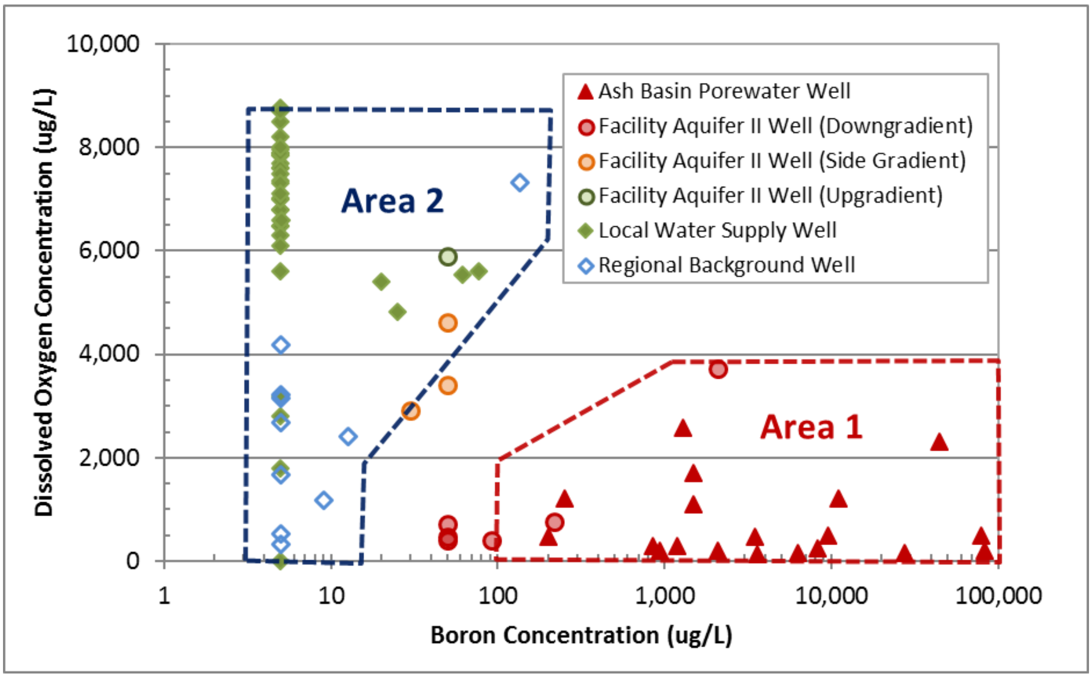


Figure 7: Correlation plot for boron and dissolved oxygen

Step 5 – Piper plot assessment: Sulfate, chloride, and calcium are key CCR constituents and are also major ions in groundwater. CCR-impacted groundwater is expected to contain elevated sulfate, chloride, and calcium concentrations and exhibit a different pattern of the major ion composition in comparison with the pattern of background groundwater. To assess the data clustering pattern, the major ion concentration data are grouped according to the method of the correlation plots, except that the facility upgradient and side-gradient well data are combined into one group. The Piper plot results are shown in Figure 8.

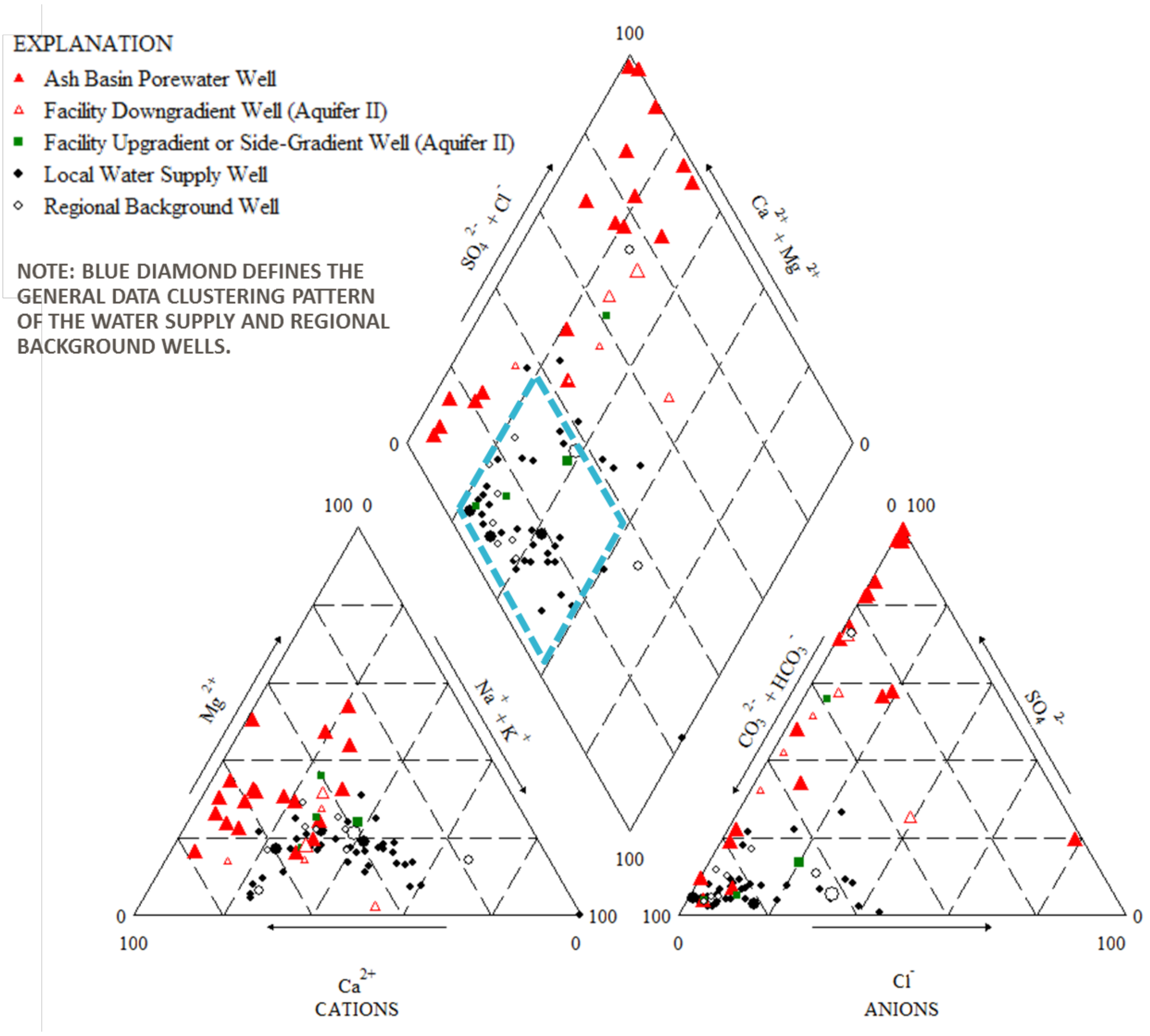


Figure 8: Piper plot of major ion concentration data from the ash basin porewater wells, facility monitoring wells in Aquifer II, local water supply wells, and regional background wells. The symbol sizes are positively correlated to the boron concentrations.

The Piper plot clearly illustrates that the local water supply well and regional background well data tend to cluster together in the area defined by the blue dashed lines, and the ash basin porewater well data tend to either have a high sulfate and chloride content and or a very high calcium content (see the diamond diagram in the central part of Figure 8). The distinct clustering pattern of the local water supply wells indicates that most of the water supply wells are not affected by CCR-impacted groundwater. There are some local water supply wells with a slightly larger symbol size; boron is detected in these wells at a concentration between 5.1 and 75 micrograms per liter (µg/L). As shown in the central diamond diagram in Figure 8, the major ion compositions for these wells are very different from other CCR-impacted facility wells in Aquifer II, indicating that groundwater in these wells are not from the ash basin system.

Note that there are some local water supply, regional background, facility upgradient or side gradient wells outside the blue diamond area, and boron concentrations in these wells are either very low or non-detects (as shown by the small symbol size). Therefore, these data points show possible variability of major ion composition in non-impacted groundwater.

<u>Step 6 – Evaluation of background conditions</u>: Because of the proximity of facility background monitoring wells to the ash basin system, the practice of using the concentrations observed in these background monitoring wells to develop the BTVs for CCR constituents is often questioned by parties that are concerned about the extent of the CCR impact. The results of the Piper plot analysis provide a basis to assess what facility background monitoring well and local water supply well data are suitable to represent background conditions. A parallel statistical analysis can then be performed to determine BTVs for other CCR constituents. The established BTVs can be further assessed by comparing with the literature values or regional BTV values if available. The comparison between the established BTVs and the local water supply well data can help determine whether water supply wells contains naturally occurring levels of inorganics or whether the detected inorganics are CCR-derived and due to migration from the ash pond system. Applying this evaluation procedure to the data of the unnamed site, it was found that the exceedances of regulatory criteria for the CCR constituents detected in the local water supply wells are considered naturally occurring and not related to the CCR impact.

<u>Step 7 – Further evaluation of the local water supply well data that show a sign of CCR impacted groundwater</u>: The data set used for the evaluation demonstration here show differentiable data clustering patterns for the local water supply wells and CCR-impacted facility wells. It is noted that a few outlier data points of the local water supply wells and the facility background wells appear to lean toward or mingle with the data points of the ash basin porewater wells and impacted facility monitoring wells (Figures 6, 7, and 8). A further evaluation to determine the possibility of CCR impact to these outlier wells is needed. Other lines of evidence can be used to assess the potential of the CCR impact for these wells. Because the locations of these outlier wells are close to other water supply wells (of similar well construction and pumping rate) that show no sign of CCR impact and the simulated groundwater flow field indicates that these wells are not downgradient of the ash basin system, these outlier wells thus are considered not impacted by the ash basin system.

CONCLUSIONS

A multi-step and multiple-line-of evidence approach has been developed to evaluate the extent of the CCR impact from an ash basin pond system to nearby local water supply wells. The approach uses common statistical tools and diagnostic plots to help determine whether a local water supply well contains naturally occurring levels of inorganics or whether the detected inorganics are CCR-derived and due to migration from an ash pond system. The approach has been successfully applied to several CCR-impacted sites and is expected to help diagnostic evaluation for many other CCR sites.

REFERENCES

[1] USEPA. 2015. Coal Combustion Residual (CCR) Rule (Hazardous and Solid Waste Management System; Disposal of Coal Combustion Residuals from Electric Utilities; FR 80(74): 21302-21501, April 19, 2015. U.S. Environmental Protection Agency.

[2] USEPA. 2013. Statistical Software ProUCL 5.0.00 for Environmental Applications for Data Sets with and without Nondetect Observations. Software: http://www2.epa.gov/land-research/proucl-software, and User's Guide: http://www2.epa.gov/sites/production/files/2015-03/documents/proucl_v5.0_user.PDF

[3] Domenico, P.A. and Schwartz, F.W. 1998. Physical and chemical hydrogeology (Vol. 44). New York: Wiley.

[4] Briel, L.I. 1997. Water quality in the Appalachian Valley and Ridge, the Blue Ridge, and the Piedmont physiographic provinces, eastern United States (No. 1422-D). US Geological Survey.

[5] USEPA. 1980. Effects of Coal-ash Leachate on Ground Water Quality. EPA-600/7-80-066. March.

[6] Cunningham, W.L. and Daniel, C.C. 2001. Investigation of ground-water availability and quality in Orange County, North Carolina (No. 4286). US Department of the Interior, US Geological Survey.