# Methodology for Predictive Groundwater Quality Compliance Analysis with Focus on Cobalt, Lead, Lithium, and Molybdenum

# Nathaniel R. Keller<sup>1</sup>, Eric J. Tlachac<sup>1</sup>, Stuart J. Cravens<sup>2</sup>

<sup>1</sup>Natural Resource Technology, Inc., 234 W. Florida St, Milwaukee, WI 53204; <sup>2</sup>Natural Resource Technology, Inc., 2422 E. Washington Street, Suite 104, Bloomington, IL 61704

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### **ABSTRACT**

This paper presents a methodology developed for early prediction of CCR unit compliance with the groundwater quality requirements of USEPA's Final Rule on Disposal of CCR from Electric Utilities (40CFR257) by comparing constituent concentrations in background wells to downgradient concentrations prior to completion of the background monitoring period. A tabular heat mapping approach utilizes color-coding coupled with simplified statistical evaluation techniques to predict and visually communicate CCR unit compliance status to facility operators. Early prediction of compliance status is critical in assisting utilities in the decision-making process to determine and prioritize which CCR units at a facility will have to be either closed, retrofitted, or undergo corrective action to remediate groundwater.

Specific focus is placed on the four Appendix IV compounds that do not have federal Maximum Contaminant Levels (MCLs) – cobalt, lead, lithium, and molybdenum. Establishing an appropriate background concentration for these four trace metals and identifying their source is critical to ensure compliance with the CCR Rule. Data from the Uppermost Aquifer at 35 CCR Units in the Midwest were evaluated to determine if concentrations of these trace metals correlate with other indicators of CCR impacts included in Appendix III. Each site was assessed separately and results combined to determine what (in addition to the CCR unit) may affect the concentrations of cobalt, lead, lithium, and molybdenum in groundwater (i.e. aquifer materials, geochemical conditions, etc.). A brief summary of the fate and transport of each of these compounds, CCR sources, anthropogenic sources, and potential natural sources is included.

### BACKGROUND AND OBJECTIVES

The USEPA's Final CCR Rule (40 CFR Part 257) requires the collection of eight independent samples from groundwater monitoring systems for existing CCR landfills and surface impoundments by October 17, 2017 to establish background values for the monitored parameters listed in Appendices III and IV to Part 257 (40CFR 257.94(b)). Future compliance with the groundwater monitoring requirements of the CCR Rule is based partially on these background values, as the compliance metrics to which observed downgradient values are compared for evaluation of Statistically Significant Increases (SSIs) are these background values for the Detection Monitoring program (Appendix III), and the greater of these background values and the USEPA Maximum Contaminant Level (MCL) where established (referred to as the Groundwater Protection Standard) for the Assessment Monitoring program (Appendix IV).

Since SSIs can be one of multiple triggers for CCR unit closure contained in the CCR Rule, early evaluation of this data as it is collected facilitates comprehensive compliance planning for existing units as information is gathered to determine compliance with the other requirements that have closure triggers (e.g., location restrictions, stability criteria, etc.). Such evaluation also facilitates early planning for groundwater corrective action if the data indicates it will be required.

Presented herein is an example of early evaluation of groundwater quality data with the objective of predicting CCR unit compliance. There is specific focus upon the four Appendix IV parameters that do not have MCLs: cobalt, lead, lithium, and molybdenum. Since these may be naturally-occurring or from upgradient anthropogenic sources, establishing appropriate background concentrations is an important part of establishing compliance with the groundwater quality requirements of the CCR Rule. This paper presents an initial overview of these parameters and their occurrence in the uppermost aquifer at 35 CCR units and multi-units in the Midwest.

Early evaluation of the water quality data collected during the background monitoring period in conjunction with groundwater elevation data also facilitates verification of upgradient/background and downgradient designations for the groundwater monitoring systems. The design of these monitoring systems may have been based upon little previous groundwater monitoring data, particularly for surface impoundments not previously monitored (with respect to groundwater quality), and, where previous monitoring was conducted, such as for a state regulatory agency, the hydrogeologic unit being monitored may have differed from the uppermost aquifer due to variation in monitoring requirements between the CCR Rule and applicable state rules. Early evaluation of this data during the background monitoring period allowed for any necessary changes in upgradient/background and downgradient designations, and even installation of additional monitoring wells where required.

### **METHODOLOGY**

Parameter values observed in samples from upgradient/background monitoring wells were compared to parameter values observed in samples from downgradient monitoring wells following each round of sampling.

For the first two rounds of sampling, maximum parameter values between upgradient/background wells and downgradient wells were compared, and professional judgement was utilized to identify downgradient values that were significantly higher than upgradient. Color-coding was used to help quickly communicate this information on summary tables of water quality data (Figure 1).

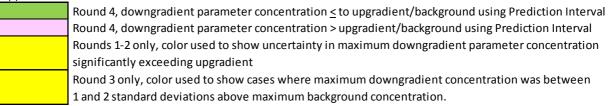
Starting with the third round of sampling, the standard deviation of parameter values was incorporated into the evaluation. Where the maximum downgradient parameter value in the monitoring system for the third round of sampling was less than the maximum upgradient/background parameter value for all rounds of sampling plus one standard deviation, the CCR unit was considered to be compliant with the CCR Rule groundwater quality requirements for that parameter. Where greater, the CCR unit was considered to be potentially non-compliant for that parameter. Where the maximum downgradient parameter value for the third round of sampling was greater than the maximum upgradient/background parameter value for all rounds of sampling plus two standard deviations, the CCR unit was considered to be most likely non-compliant for that parameter.

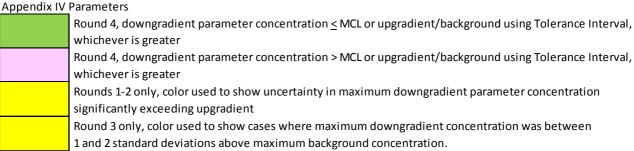
More robust statistical methods were applied to the datasets starting with the fourth round of sampling. The downgradient parameter values observed in each well sampled during that round were individually compared to a statistical background value calculated for each monitored parameter using the Electric Power Research Institute's (EPRI's) MANAGES Groundwater Data Management Software (Version 3.4). The entire upgradient/background parameter dataset, including parameter values from all upgradient/background wells, was used to calculate the background values (interwell comparison), but the way the values were calculated varied between the parameters. A prediction interval was calculated for Appendix III parameters and the upper limit of that interval was used as the background value for all parameters except pH, where both the upper and lower limits of the prediction interval were used. A tolerance interval was calculated for Appendix IV parameters, and the upper limit was considered to be the background value. However, the background value was only compared to downgradient parameter values without an MCL (cobalt, lead, lithium, and molybdenum) or if it exceeded the MCL; otherwise, the MCL was compared to downgradient parameter values. Prediction and tolerance interval calculations were parametric where the dataset was normally distributed with a low frequency of non-detects (for parameters with concentrations determined by analytical laboratories). Calculations were non-parametric where the dataset was not normally distributed and/or had a high frequency of nondetects.

Daviero et a va /Tatal\	Heat Map							
Parameters (Total)		R1	R2	R3	R4-Meth1	R4-Meth 2		
Appendix III					Pred Int	Tol Int		
Boron					0.024			
Calcium					42.82			
Chloride					18.2			
Fluoride					0.343			
Sulfate					95.5			
TDS					300			
pH-Field					5.49 / 7.26			
Appendix IV								
Antimony						0.0006		
Arsenic						0.0285		
Barium						0.0409		
Beryllium						0.0005		
Cadmium						0.0002		
Chromium						0.0026		
Cobalt						0.0002		
Fluoride						4.136		
Lead						0.0006		
Lithium						0.1299		
Mercury						0.00005		
Molybdenum						0.0612		
Selenium						0.0009		
Thallium						0.0002		
Radium 226/228						1.14		

### **Heat Map Color Scale:**

Appendix III Parameters



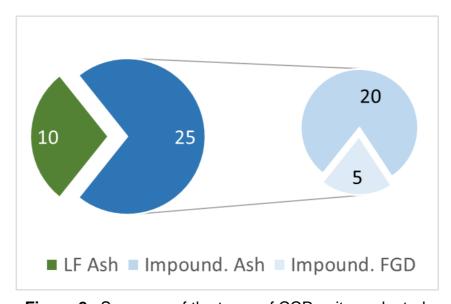


**Figure 1.** Example of color coding used to communicate compliance prediction.

The statistical methods employed were simplified to minimize analysis time since these were compliance predictions, not determinations, and the datasets were limited. For example, statistics were only applied on upgradient/background parameter values; individual downgradient parameter values for the most recent round of sampling were compared to the calculated statistical background values. For compliance determinations, statistics would also be applied to all downgradient parameter values. Also, emphasis was placed on compliance threshold exceedances for Appendix IV parameters. While prediction of compliance status for Appendix III parameters (Detection Monitoring) was evaluated, it was not used as a basis to determine whether Appendix IV compliance predictions (Assessment Monitoring) were necessary.

### **OBSERVATIONS**

General observations made from these CCR unit compliance predictions are based upon a database of 35 CCR units and multi-units located in the Midwest. Ten of these units are landfills and the remaining are surface impoundments (Figure 2). Five of the 25 impoundments contain flue-gas desulfurization (FGD) sludge and the rest contain coal ash.



**Figure 2.** Summary of the types of CCR units evaluated.

Twenty of the units and multi-units are considered to be lined and 15 unlined. A unit was considered lined if it has a liner constructed of at least one (or a combination) of the following: compacted clay, geomembrane, or concrete.

With regard to hydrogeologic setting, the uppermost aquifer is unlithified soils at 30 of the units and multi-units, and bedrock at five.

Correlation was observed in compliance status between Appendix III and Appendix IV parameters. Greater than 75% of the units and multi-units evaluated had downgradient

parameter values significantly greater than the Groundwater Protection Standard (GWPS) for at least one Appendix IV parameter if they also had downgradient parameter values significantly greater than calculated background parameter values for at least one Appendix III parameter. This suggests that an alternate source demonstration or corrective action will likely be necessary if Assessment Monitoring is triggered during Detection Monitoring.

For cobalt, lead, lithium, and molybdenum, which do not have established MCLs, 75% of the units and multi-units evaluated had downgradient parameter concentrations greater than the GWPS (upper limit of the calculated background tolerance interval). This suggests that these four parameters will be significant to CCR unit groundwater compliance going forward.

## FURTHER EVALUATION OF COBALT, LEAD, LITHIUM, AND MOLYBDENUM

Concentrations of cobalt, lead, lithium, and molybdenum were compiled and evaluated to determine: 1) co-occurrence of these trace metals and Appendix III indicators of CCR impacts; and 2) if these co-occurrences correlate or are coincident with these indicators, physical characteristics of the unit, and site hydrogeology.

Boron and sulfate were selected as Appendix III parameters for correlation or coincidence because they commonly indicate groundwater has been impacted by CCR<sup>1,2</sup>. In order to evaluate the occurrence of the cobalt, lead, lithium, and molybdenum, and their potential correlation/coincidence with Appendix III parameters, unit construction, and geologic setting, CCR units were classified as shown in Table 1. An initial assessment was performed to evaluate the occurrence of cobalt, lead, lithium, and molybdenum, as well as the selected Appendix III CCR indicators (boron and sulfate). Box plots were prepared for each of the parameters following evaluation of non-detect values. The percentage of non-detect values was plotted for each classification to determine if the occurrence of parameters were correlated with any of the classifications. Box plots were also prepared using all data (1,083 individual samples) and classifications with non-detect values plotted at half of the detection limit. Box plots were used to assess whether elevated concentrations were coincident with particular unit characteristics or site geology.

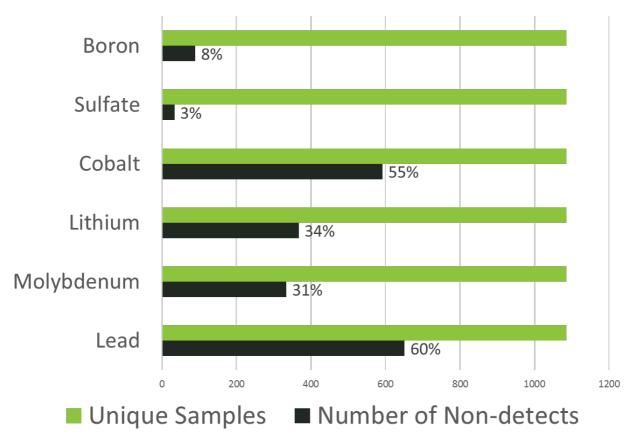
Following the evaluation of occurrence with unit classifications, downgradient concentrations of cobalt, lead, lithium, and molybdenum were compared to the background concentrations calculated as part of the compliance prediction. The objective was to determine if downgradient exceedances of the background concentrations for these four parameters were coincident with downgradient exceedances of background concentrations for boron and/or sulfate. Coincident exceedances (100%) are interpreted to indicate that the Appendix IV exceedances downgradient are likely related to the CCR Unit. Two of the units and six upgradient wells (at 6 units) were included in the analysis of parameter occurrence, but not included in the evaluation of parameter coincidence because upgradient wells were affected by offsite impacts.

Table 1. Summary of CCR Units and Site Hydrogeology included in Database

Statistical Unit ID	Background Wells	Downgradient Wells	Construction Details	Unit Type	Type of CCP	Geologic Setting	Upgradient Source
NA	2			Surface Impoundment	Ash	Unlithified sand	Yes
1 2		5	Halinad	Inactive Surface	Ash	I Inlithified cond	
1	2	5	Unlined	Impoundment	ASII	Unlithified sand	
2	2	5	Lined	Surface	FGD	Unlithified sand	
_				Impoundment Surface			***************************************
3	2	4	Lined	Impoundment	FGD	Unlithified sand	
4	3	5	Lined	Landfill Surface	Ash	Unlithified sand	
5	2	4	Unlined	Impoundment	Ash	Unlithified sand	
6	2	9	Lined	Landfill Surface	Ash	Unlithified sand	
7	2	4	Lined	Impoundment	FGD	Unlithified sand	
8	2	4	Lined	Landfill	Ash	Unlithified sand	
9	2	4	Lined	Surface Impoundment	Ash	Unlithified sand	
10	2	4	Unlined	Surface	Ash	Unlithified silt and	
				Impoundment Surface		Clay/Rock interface Bedrock	
11	2	4	Unlined	Impoundment	Ash	Shale/Limestone	
12	2	7	Unlined	Surface Impoundment	Ash	Bedrock	
12	2		Linad	Surface	Λ a.b.	Shale/Limestone	
13	2	5	Lined	Impoundment	Ash	Unlithified sand	
14	3	4	Unlined	Landfill Inactive	Ash	Unlithified sand	
15	3	4	Unlined	Surface	Ash	Unlithified sand	
				Impoundment Surface			
16	3	4	Unlined	Impoundment	Ash	Unlithified sand	
17 2	2	6	Unlined	Inactive Surface	Ash	Unlithified sand	
	2			Impoundment		Jimanneu sanu	
18	2	4	Lined	Surface	Ash	Unlithified sand	
	***************************************			Impoundment Inactive	***************************************		
19	3	4	Unlined	Surface	Ash	Unlithified sand	
				Impoundment Surface			
20	2	6	Unlined	Impoundment	Ash	Unlithified sand	
21	2	4	Unlined	Surface Impoundment	Ash	Unlithified sand	
22	2	4	Lined	Landfill	Ash	Unlithified sand	
23	2	5	Unlined	Surface	Ash	Unlithified sand	
	_	_		Impoundment Surface			
24	2	6	Unlined	Impoundment	Ash	Unlithified sand	
25	2	6	Lined	Landfill Surface	Ash	Unlithified sand	
26	1	4	Lined	Impoundment	FGD	Unlithified sand	
27	3	4	Lined	Surface Impoundment	Ash	Unlithified sand	
28	4	11	Lined	Landfill	Ash	Bedrock Limestone/	
29	1	3	Lined	Surface	FGD	Shale Unlithified sand	
NA	1	4	Lined	Impoundment Surface	Ash		Yes
				Impoundment Surface		Unlithified sand	162
30	2	4	Lined	Impoundment	Ash	Unlithified sand	
31	3 2	4	Lined Lined	Landfill Landfill	Ash Ash	Unlithified Sand Bedrock Dolomite	
32	2	1	Lined	Landfill	Ash	Unlithified Sand	
33	2	4	Lined	Landfill	Ash	Bedrock Dolomite	

NA - Unit not included in statistical analysis due to upgradient source

The relative frequency of non-detect results is displayed in Figure 3. The Appendix III indicator parameters boron and sulfate were non-detect in less than 10% of the samples. Appendix IV parameters of interest were non-detect in greater than 30% of the samples, and lead was the least detected of the 4 parameters.



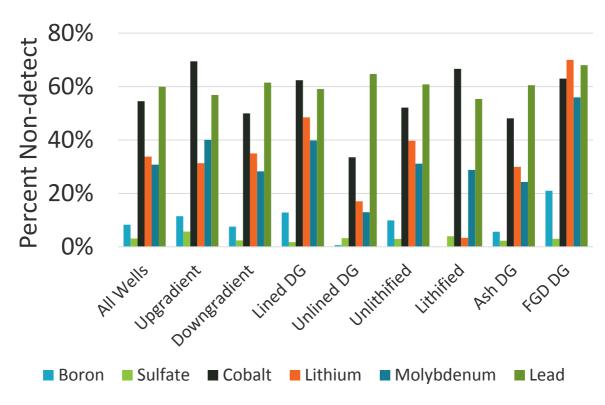
**Figure 3.** Summary of non-detect results for boron, sulfate, cobalt, lithium, molybdenum, and lead.

Further characterization of the occurrence of cobalt, lead, lithium, and molybdenum was performed with regard to position of the well in the monitoring system (upgradient versus downgradient) as well as each of the unit classifications listed in Table 1. The percentage of non-detect values for each of the classifications is included in Figure 4.

The following was observed based on the classifications of the units:

- The percentage of non-detects in upgradient wells was generally higher than downgradient wells, with the exception of lithium and lead
- Units that are lined generally had a higher percentage of non-detects than unlined units, with the exception of lead and sulfate
- Lithium was detected more frequently at unlined units and/or in lithified aquifers

 Cobalt and molybdenum were detected more frequently at unlined and/or ash units (as opposed to FGD)

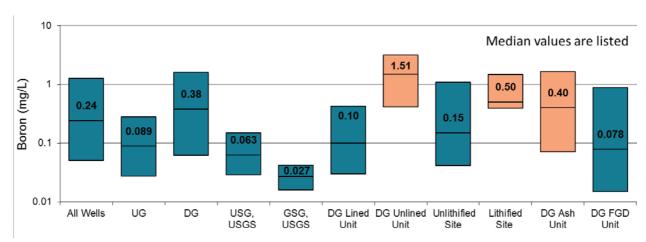


**Figure 4.** Percentage of non-detect results based on CCR unit classifications and well positions (DG= downgradient wells).

The underlying causes for these observations were not fully evaluated, but observations that unlined sites result in less non-detect results are not unexpected. Reasons for more frequent detection of lithium in lithified aquifers are not readily apparent, but may be related to aquifer composition or geochemical conditions.

# OCCURRENCE OF APPENDIX III PARAMETERS (BORON AND SULFATE)

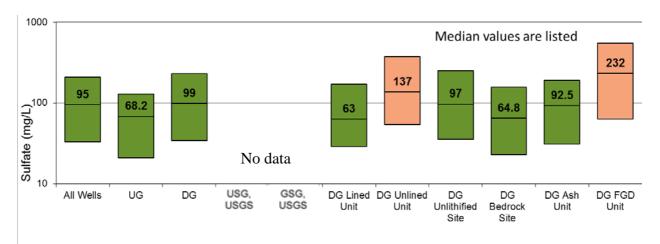
Boron and sulfate concentrations were also evaluated with regard to position of the well in the monitoring system and the unit classifications included in Table 1, and box-plots were prepared to compare the distribution of concentrations. Non-detect values were included in the plots at half the value of the detection limit. The box-plot for boron is displayed in Figure 5, and the summary for sulfate is shown on Figure 6. Background (naturally-occurring) values were also included for unconsolidated sand and gravel aquifers (USG), and glacial unconsolidated sand and gravel aquifers (GSG)<sup>3</sup> for reference.



**Figure 5.** Box-plot of boron concentrations based on CCR unit classifications and well positions (UG= upgradient wells, DG= downgradient wells).

As displayed in the plot, boron concentrations were highest downgradient at unlined units and, in general, wells downgradient of ash units or in lithified aquifers had elevated concentrations with respect to background.

Sulfate concentrations were also elevated downgradient of unlined units, but the highest concentrations were measured downgradient of FGD units. The lowest concentrations of sulfate were measured downgradient of lined units and/or wells screened within lithified aquifers. This may be related to anoxic conditions and reduction of sulfate occurring below and downgradient of these units.



**Figure 6.** Box-plot of sulfate concentrations based on CCR unit classifications and well positions (UG= upgradient wells, DG= downgradient wells).

### OCCURRENCE OF COBALT, LEAD, LITHIUM, AND MOLYBDENUM

Box-plots were also created to evaluate the distribution of selected Appendix IV parameters following the same procedures performed for boron and sulfate. The results

of the analysis are shown in Figures 7-10. A summary of observations for each parameter includes:

### Cobalt

- Median concentrations of cobalt were lowest in lithified aquifers, consistent with these units also having over 60% non-detect results
- The highest concentrations were detected downgradient of FGD units

### Lithium

- Median concentrations were highest downgradient of unlined units, and in lithified aquifers, consistent with a lower percentage of non-detect values
- Concentrations are similar to those detected in non-CCR unconsolidated sand and gravel aquifers<sup>3</sup>

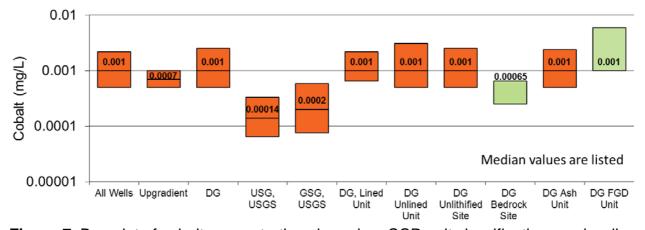
# • Molybdenum

- Median concentrations are elevated downgradient of unlined units and/or units with ash, and wells screened within lithified aguifers
- Median concentrations are lowest in upgradient wells and wells downgradient of FGD units

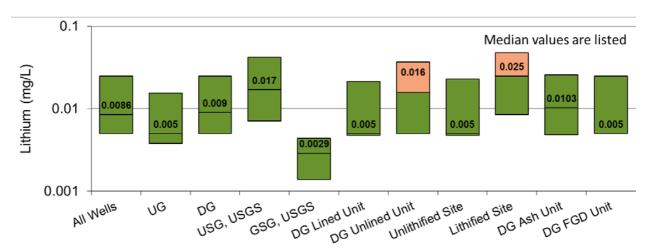
### Lead

- Large percentages of non-detect results are present for lead and no apparent correlations were observed
- In general, concentrations of lead detected downgradient of CCR units were below those detected in non-CCR unconsolidated sand and gravel aquifers<sup>3</sup>

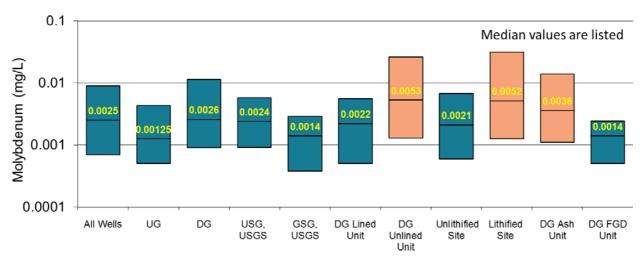
Explanations for these observations have not been fully developed, but, in general, the distributions are controlled by a complex combination of geochemical conditions and reactions, source material and concentrations, unit construction, and aquifer composition.



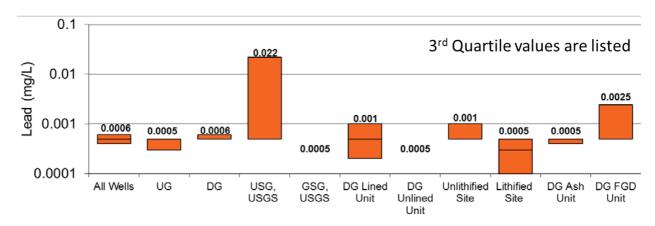
**Figure 7.** Box-plot of cobalt concentrations based on CCR unit classifications and well positions (UG= upgradient wells, DG= downgradient wells).



**Figure 8.** Box-plot of Lithium concentrations based on CCR unit classifications and well positions (UG= upgradient wells, DG= downgradient wells).



**Figure 9.** Box-plot of molybdenum concentrations based on CCR unit classifications and well positions (UG= upgradient wells, DG= downgradient wells).



**Figure 10.** Box-plot of lead concentrations based on CCR unit classifications and well positions (UG= upgradient wells, DG= downgradient wells).

# EVALUATION OF APPENDIX III AND APPENDIX IV COINCIDENT EXCEEDANCES

If Appendix IV parameters exceed the GWPS, which is the greater of the MCL (where established) or background concentrations, additional monitoring, an Alternate Source Demonstration, and/or Corrective Action is required. Cobalt, lithium, lead, and molybdenum have no MCLs and very low concentrations can result in additional assessment if those concentrations are elevated with respect to background. The following evaluation is a preliminary review of the selected Appendix IV exceedances to assess whether they correspond to the CCR indicators boron and sulfate. Initially all data was pooled to assess which Appendix IV exceedances coincided with Appendix III exceedances. The results are included in Figure 11. Molybdenum exceedances coincided most frequently with boron (54%) and sulfate (28%). Lead exceedances rarely coincided with either boron or sulfate, while cobalt exceeded coincident with boron (19%) and sulfate (21%) at about the same percentage, and lithium more frequently exceeded coincident with boron (28%).

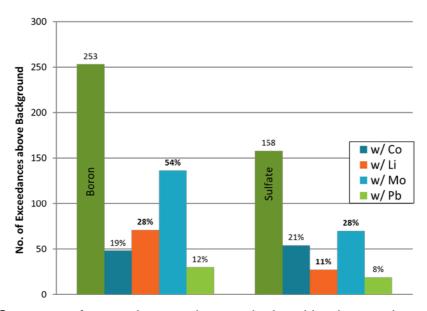
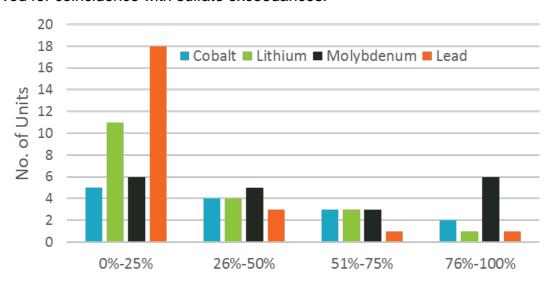


Figure 11. Summary of exceedances above calculated background concentrations

Further evaluation was completed to determine CCR unit-specific exceedance coincidence (versus sample-specific). Unit-specific assessments were completed to more effectively evaluate the percentage of exceedances that coincided with boron (Figure 11) or sulfate (Figure 12). High percentages of coincident exceedances at a unit indicate the exceedances for Appendix IV parameters are likely a result of impacts from the CCR unit. In contrast, a low percentage of coincident exceedances may indicate an alternate source or geochemical conditions and reactions are controlling the concentrations of the Appendix IV parameters.

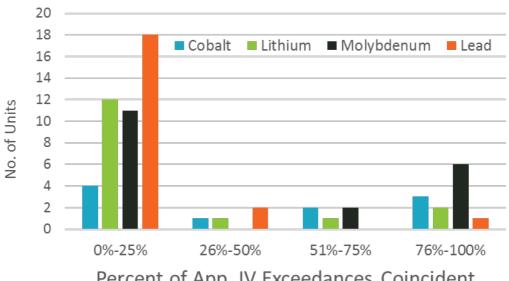
At units where the coincident exceedances are greater than 50%, the Appendix IV exceedances are likely related to the CCR unit. Molybdenum exceedances coincident

with boron (>50%, 9 of 20 units) suggest that it is most often frequently related to a CCR unit. However, cobalt (5 units), lead (2 units), and lithium (4 units) exceedances are less often coincident with boron, indicating that the CCR unit may not be the source of increased downgradient concentrations of these parameters. Similar trends were observed for coincidence with sulfate exceedances.



Percent of App. IV Exceedances Coincident with Boron (Site Based)

**Figure 12.** Summary of CCR units with percentage of exceedances coincident with boron.



Percent of App. IV Exceedances Coincident with Sulfate (Site Based)

Figure 13. Summary of CCR units with percentage of exceedances coincident with sulfate.

### CONCLUSIONS

Early evaluation of groundwater quality data collected from existing CCR units during the background monitoring period can facilitate preliminary compliance predictions for these units. This information can be helpful to unit owners and operators as they develop compliance strategies.

Early evaluation of this data was also helpful to verify the adequacy of the monitoring networks, and make any necessary adjustments during the background monitoring period.

Evaluation of groundwater data collected at 35 CCR units located in the Midwest and of varying construction, hydrogeologic setting, and CCR type using statistical methods applied to the data from the upgradient/background wells following the first four rounds of sampling in the background monitoring period revealed the following trends:

- Greater than 75% of the units and multi-units evaluated had at least one Appendix IV parameter exceedance if they had at least one Appendix III parameter exceedance, suggesting that an alternate source demonstration or corrective action will likely be necessary if Assessment Monitoring is triggered during Detection Monitoring
- 75% of the units and multi-units evaluated had downgradient parameter concentrations greater than the GWPS for cobalt, lead, lithium, and molybdenum, which is the calculated background concentration since these four parameters do not have an established USEPA MCL, suggesting that these four parameters will be significant to CCR unit groundwater compliance going forward
- When the percentage of non-detects, position in the monitoring system, CCR unit type and construction, and hydrogeologic setting were further evaluated for cobalt, lead, lithium, and molybdenum:
  - The percentage of non-detects in upgradient wells was generally higher than downgradient wells, with the exception of lithium and lead
  - Units that are lined generally had a higher percentage of non-detects than unlined units, with the exception of lead and sulfate
  - Lithium was detected more frequently at unlined units and/or in lithified aquifers
  - Cobalt and molybdenum were detected more frequently at unlined and/or ash sites (as opposed to FGD)

- When coincident exceedances of Appendix III parameters boron and sulfate, which are commonly associated with CCR impacts, and Appendix IV parameters cobalt, lead, lithium, and molybdenum were evaluated:
  - Molybdenum exceedances coincided most frequently with both boron and sulfate
  - Cobalt, lead, and lithium exceedances are less frequently coincident with boron and sulfate
  - At least half of the units had less than 50% coincidence between Appendix III (boron and sulfate) and Appendix IV parameters. indicating cobalt, lithium, molybdenum, and lead are frequently detected above background without corresponding increases of boron or sulfate. At these units detailed evaluations need to be performed to identify the source of increases in cobalt, lithium, molybdenum, and lead.

### REFERENCES

- [1] EPRI, Groundwater Quality Signatures for Assessing Potential Impacts from Coal Combustion Product Leachate, Palo Alto, CA, 2012, 162 p.
- [2] EPRI, Characterization of Field Leachates at Coal Combustion Product Management Sites Arsenic, Selenium, Chromium, and Mercury Speciation, Palo Alto, CA, 2006, 188 p.
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