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# Introduction

## Background

*The following was taken from the project description provided by EPRI and adapted:*

In the US, a common practice at coal-fired steam-electric power plants in the 1960s through the 2000s was to manage coal ash in impoundments, often unlined. This design allowed inorganic elements to leach into groundwater under and around the management units. Recent regulations in the United States now require utilities to close these unlined management units and remediate sites where inorganic elements have leached to groundwater.

There are two methods commonly used to prevent future leaching. The first of these,

closure by removal, has the advantage of permanently removing the source so there is no potential for future leaching. Still, it has the disadvantage of being more geochemically disruptive and taking longer to implement than closure in place. The second is closure in place where the impoundment is dewatered and covered with soil or geosynthetic cap.

This project seeks to evaluate the effect that each of these closure options has on concentrations of the inorganic elements in groundwater. Data collected for this project was measured at 18 impoundments from various locations in the United States. For each impoundment, the date operation ceased, and the dates closure began and completed were summarised. Groundwater data from monitoring wells near the ponds have been compiled from before, during, and after the closures to provide a basis for evaluation.

## Project Scope

This project is focused on how groundwater quality around powerplant disposal sites is impacted over time. We will take a comparative approach to study how different closure methods of CCP ponds affect leachate conditions. We will also investigate how initial groundwater conditions determine resultant changes in water quality post-closure and how this changes over time. We will perform this analysis at the pond level, providing novel insights differentiating from current well-based procedures. Analyses were restricted to a subset of measurements identified by EPRI as chemicals of environmental concern and measurements of interest that are indicative of local geochemistry.

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# The Data

## Initial Data

The initial data provided by EPRI consists of 10 excel files split across wells and a table explaining site information such as closure method which was extracted from a .ppt file slide. The excel files contained different formats of headers and orders of these columns, which was handled during data cleaning (see Cleaning\_script.R in ‘notebooks’).

Table 1: Example of data provided in original .xlsx files. Note: Mocked up data.

| **EPRI site ID** | **Well Mask** | **chemical** | **units** | **non-detect flag** | **analytical result** | **sample\_date** |
| --- | --- | --- | --- | --- | --- | --- |
| 10999 | 10999-1X | Boron | mg/L | < | 0.01 | 05-May-16 |
| 10999 | 10999-1AU | pH | AU |  | 7.62 | 05-May-16 |

Table 2: Data dictionary of initial .xlsx data uploads.

| **Header Name** | **Data Description** |
| --- | --- |
| EPRI\_ID | A 5 digit number taking the form XXXXX being the site ID, |
| well\_mask | A unique identifier for each well taking the form XXXXX-YA. The 5 digit corresponds to EPRI\_ID. The Y prefix of a number indicates the pond number at the site. The letter(s) (A) following are the well unique identifiers. A ‘U’ in the entry indicated the well was an upgradient well. |
| sample\_date | Date the measurement was taken. |
| measurement | The type of measurement taken. This takes the form of chemical concentration readings and other geochemical readings such as pH or temperature. |
| units | Denoting the units of the associated measurement. |
| analytical\_result | The numeric value of the measurement taken. |
| non.detect\_flag | ‘<’ is placed in rows that are below the detection threshold limit for that particular measurement, indicating the analytical\_result at this row position is below the inserted number. |

## Pond information:

Table 3: Example of data provided in original .ppt files. Note: Mocked up data

| **EPRI ID** | **Pond** | **Year stopped receiving waste** | **Year closure construction started** | **Year closure completed** | **Closure method** |
| --- | --- | --- | --- | --- | --- |
| 10999 | 1 | 2014 | Aug-15 | Oct-20 | CBR |
| 12345 | 1 | 1985 | 2013 | 2014 | CIP |

The information provided from the .ppt slide included the EPRI ID matching the EPRI\_ID ‘XXXXX’ number in these excel sheets. A second row (pond) denoted the pond number at these sites, equivalent to the well\_mask ‘pond’ number. This data table also included the closure method (CIP or CBR) and dates (either in month-year or year-only format) of when waste was last received at the pond, when closure started and when it was completed.

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# Final Data Structure(s)

## Data Cleaning

The code built as part of the delivery of this project is annotated thoroughly for step-by-step walkthroughs of the data cleaning and analysis pipeline. Below is an overview of the major methodological steps performed and an explanation of assumptions and decisions made in handling these steps.

1. **Reading in and collating excel files into a contiguous dataset.**

As the excel files could have different column names and orders between them, files were read into R using an agnostic method, renaming and reordering columns based on patterns common to all files. These individual files were then combined into a large data frame containing the information from all 10 original files.

1. **Creation of new features by breaking apart well\_mask into pond and well identifiers**

The well\_mask variable was split into several new features: site ID, pond number, and the unique well identifier (UI).

1. **Joining of excel data to pond data provided from .ppt file**

The data around the site, pond closure method and construction dates were joined using the EPRI\_ID and pond number.

1. **Filtering out of any out-of-tolerance values**

Some pH values deemed impossible (>14) were removed from the dataset; all other outliers were kept in the analysis.

### Initial Dataset Explorations

The dataset provided consisted of 18 ponds, 12 closure by removal (CBR) ponds, and 6 closure in place (CIP) ponds. Each pond had different numbers of wells built/ data collected from. Summaries of this can be seen in Fig. 1 and Fig. 2. All bar two of these ponds had information available for when waste was last received, when closure construction started, and when the closure was complete. Pond 13416\_2 and 10181\_1 are missing data on when construction started and when waste was last received, respectively. However, the distribution of timepoints at which sampling was undertaken results in additional ponds without data around these events. In total, there are 8 ponds (5 CBR, 3 CIP) for which boron levels are tracked through the period of time over which waste stops being received, and 12 ponds (9 CBR, 3 CIP) for which boron levels are monitored across the start of closure. This is less of an issue for closure completion dates. Furthermore, as the sampling frequency varies between different measured chemicals, the number of ponds in which there is data at closure or waste-stopped events depends on the chemical of interest. Boron was sampled most frequently, and is represented most at these events across ponds.

Most of these data are accurate to the year, with some dates being given in full month/day/year format as is standard in the USA.

The data has large amounts of sampling variability in terms of dates sampled post-closure, the number of wells present at sites, and which measurements are captured across these ponds. The well numbers show large variation as the minimum number is 5 wells present at 17019\_2, the max is 198 wells present at 33449\_1 and the median is 14 wells (Fig. 1 and 2).

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| Fig. 1: Boxplot of the number of wells around each pond for each closure type |

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| Fig. 2: Barchart of the number of wells present at each pond for each closure type |

The closure method in Table 4 is filled in with the colour used to denote its associated visualisations. As this clearly highlights, more ponds underwent CBR compared to CIP. Fig. 3 and Fig. 4 show comparisons of how much data was collected for CBR ponds compared to CIP ponds post closure.

​Table 4: Summary of key closure dates for each pond

| **EPRI ID** | **Pond** | **Year stopped receiving waste** | **Year closure construction started** | **Year closure completed** | **Closure method** |
| --- | --- | --- | --- | --- | --- |
| **17019** | 1 | 2015 | 08/16/22 | 10/21/22 | CIP |
| **17019** | 2 | 2015 | 2017 | 2018 | CBR |
| **13416** | 1 | 12/11/2022 | 2015 | 06/16/22 | CIP |
| **13416** | 2 | 2000 | **NA** | 01/13/22 | CIP |
| **13667** | 1 | 06/05/2022 | 08/11/2022 | 10/12/2022 | CIP |
| **22346** | 1 | 10/18/22 | 2019 | 2019 | CBR |
| **22346** | 2 | 04/16/22 | 2019 | 2020 | CBR |
| **22348** | 1 | 04/17/22 | 2018 | 2019 | CBR |
| **33446** | 1 | 06/13/22 | 2015 | 2016 | CBR |
| **33105** | 1 | 04/13/22 | 2016 | 2020 | CBR |
| **33108** | 1 | 04/13/22 | 2015 | 2019 | CBR |
| **33449** | 1 | 01/13/22 | 2017 | 05/19/22 | CBR |
| **10181** | 1 | **NA** | 11/19/22 | 2021 | CBR |
| **10168** | 1 | 1971 | 2016 | 2020 | CBR |
| **10172** | 1 | 1966 | 2016 | 2017 | CBR |
| **10172** | 2 | 2015 | 2018 | 2018 | CBR |
| **17154** | 1 | 01/20/22 | 2020 | 09/21/22 | CIP |
| **13114** | 1 | 1993 | 1994 | 1994 | CIP |

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| Fig. 3: Boxplot of the number of years of sample data post closure for each closure type |

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| Fig. 4: Barchart of the number of years of sample data post closure for each closure type |

The range of post-closure dates available rounded to the nearest year also show variation. They range from less than 1 year (pond 17019\_1) to 15 years (pond 13114\_1), while the median value is 3 years (Fig. 3, 4).

There are 39 distinct measurements present in the dataset. These consist mainly of chemical concentration measurements measured in mg/L or micro g/L. Other measurements such as pH, dissolved oxygen and temperature all have the appropriate units. EPRI highlighted in their kick-off materials that there are a subset of measurements of greatest interest to EPRI, these are focused on in this report. The measurements can be grouped into two separate categories: measures of environmental concern and geophysical condition measurements. These are as follows (arranged in alphabetical order, not by priority):

**Measurements of environmental concern highlighted as the highest priority by EPRI:**

Arsenic, Antimony, Boron, Chromium, Cobalt, Lithium, Molybdenum, Selenium.

**Other measurements of interest detailing geophysical conditions:**

Calcium, Chloride, Dissolved Oxygen, Iron, Manganese, Oxidation Reduction Potential, pH, Potassium , Sodium, Sulfate, Temperature.

### Combining Time Series Well Information

Each pond has several wells positioned “upgradient” and “downgradient” to the pond. Different chemical measurements were taken sporadically from these wells for each pond. To determine the general trend and remove the impact of potentially anomalous well readings, these well readings were aggregated into a pond reading for each data point. For each pond and measurement type, wells were separated based on whether they were labelled upgradient or downgradient. For each data point where wells were sampled, the well readings were aggregated, and the median reading was used.

We attempted advanced statistical methods to smooth this data to lessen the impact of sample points where the groundwater chemical composition was dramatically different or where very few well readings gave a shifted median reading. We attempted methods such as local estimation of scatterplot smoothing (LOESS) and general additive models (GAM). However, the small sample size for some wells led to excessive smoothing that removed the underlying trends or prevented models such as GAM from being implemented effectively. Another approach was attempted by binning samples into half year and 4-month long bins, and aggregating measurements over these time bins. Again, odd trends were found in the data when aggregated in this manner, and the loss of time resolution potentially removed insights early on in the pipeline. In a successful implementation, the smoothing model would be used to impute values to act as a background reading for the upgradient wells in regions missing data in significant densities for other methods. In future pipelines, these methods could be revisited for ponds with large enough sample sizes and the aggregated medians selected to reduce the effect of large outliers on the aggregated measurement.

Instead, the rolling mean, with a window size of 4, was applied to the median value for the measurement. This process was applied separately to the upgradient and downgradient readings for each measurement for each pond. These results were added as new features to the cleaned well data. For some ponds, downgradient well measurements were not taken on the same day as the upgradient well measurements, which would prevent smoothing. In these cases, the missing value was imputed by taking the mean of the value on either side of the missing value. Finally, the change in gradient was calculated by subtracting the rolling median for the upgradient wells from the downgradient rolling median. This allowed further analysis and visualisation of the trends in downgradient well readings on a pond level after removing the impact of background chemicals in the groundwater, as measured by the upgradient readings.

## Limitations With Sampling

### Time series

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| Fig. 5: Density plots of boron measurements across wells for pond 13416\_2 over time. The wells are split into downgradient (left) and upgradient (right) (*plotted using sample\_density\_ridgeplots.Rmd*). |

In the above plot (Fig. 5), each ridge-line plot has a different colour and corresponds to one of the wells for the pond indicated here as an example. The shapes of the plots indicate the amount of sampling per time point, and they show that the sampling over time is uneven, especially for the upgradient wells. Missing data is problematic for time-series analyses done with state-of-the-art statistical packages such as the Python module tsfresh. Extending the amount of sampled dates and/or the number of ponds under consideration may allow to implement methodologies to impute missing data values (e.g., filling missing data values with the median value found for the other time points of the same point or for the median value found for that same time point in the other point).

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| Fig. 6: Density plots of sample times of boron measurements for each pond. The wells are split into downgradient (left) and upgradient (right). |

As noted in the figure above, well data aggregation on a pond level improves the uneven sampling data issue. However, clear differences in the time sampling distribution between ponds still remain in the data. These differences limit the comparison of the time-series trajectories between ponds, particularly when regions of the time-series with low sampling values are compared.

### Chemical Measurements

The upgradient wells of all ponds measured boron, sulphate, calcium and chloride concentrations in the groundwater (see Fig. 7 below). The sampling coverage across the upgradient wells is more heterogeneous for the rest of the chemicals and other measurements. A similar situation is observed on a downgradient level. Two particular sites that have less chemical measurements on upgradient level are ponds 13114\_1 and 10172\_1 (Fig. 8). Future studies would benefit by including ponds with fewer missing data values on chemical measurements. This would allow it to capture associated trends between chemicals while having a more extensive set of features to train models that could predict generalities on the different behaviours led by each closure method on post-closure chemical concentrations in downgradient water.

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| Fig. 7: Number of ponds in which each chemical has at least one measure in the upgradient wells (*plotted using notebooks/important\_notebooks/nb3\_upgradientPonds\_v3.ipynb*). |

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| Fig. 8: Number of chemicals for which each pond includes measurements in the upgradient wells (*plotted using notebooks/important\_notebooks/nb3\_upgradientPonds\_v3.ipynb*). |

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# Similarities Between Sites

To obtain a single chemical measurement per pond at an upgradient level, for each pond and chemical, we computed the average of all values found across all time points. With this, we assessed for similarities on a geochemistry level between the sites where ponds are located by exploring the information on the upgradient wells. This analysis was done not solely to identify interesting similarities between local geochemistry of sites, but importantly to also identify potential similarities that may be seen in downgradient trends that may be explained by the fact of being located in sites with similar geochemistry. (Note that this analysis can be found in the Jupyter notebook ‘nb\_upgradientPonds\_v3’).

| |  | | --- | | Fig. 9: Principal Component Analysis (PCA) of upgradient wells for each pond. Each dot represents a given pond (*plotted using notebooks/important\_notebooks/nb3\_upgradientPonds\_v3.ipynb*).  By looking at the first two principal components, we can see how local geochemistry is relatively specific across sites, with some ponds showing more similarities than others. This dimensionality reduction analysis was done with the upgradient pond measurements of boron, chloride, sulfate and calcium. These were selected as they are present in data on upgradient wells for all ponds. The contribution of each chemical in the spatial distribution of each pond is indicated by the arrows next to each chemical in the plot (Fig 9).  By looking at the plot, we may be tempted to define clusters of ponds based on their distribution in this space. Instead of doing this manually, we used a state-of-the-art method called HDBSCAN (Hierarchical Density-Based Spatial Clustering of Applications with Noise). We ran HDBSCAN on the PC1 and PC2 variables obtained from the dimensionality reduction of the original variables (chemicals) to obtain the clusters highlighted in Fig 10. The single-linkage clustering tree for the ponds is shown in Fig 11.   |  | | --- | | Fig. 10: Principal Component Analysis (PCA) of upgradient wells for each pond. Each dot represents a given pond which is colored according to the output from HDBSCAN based on PC1 and PC2 (*plotted using notebooks/important\_notebooks/nb3\_upgradientPonds\_v3.ipynb*). |  |  | | --- | | Fig. 11: Single linkage tree of ponds from HDBSCAN based on PC1 and PC2. Pond labels are colored in blue and red for the two clusters identified by HDBSCAN. Ponds labelled as yellow are outliers that show more site-specific geochemistry. |   However, one may wonder how robust the clusters detected by this specific methodology were, since clusters are often contingent on the methodology used. This is especially important given the small sample size of ponds. To assess this, we explored how robust the associations between ponds recovered by trying a battery of additional state-of-the-art clustering approaches. First, we tried using another dimensionality reduction algorithm - UMAP (Uniform Manifold Approximation and Projection) and running HDBSCAN based on the output of this. We additionally attempted to run HDBSCAN on the original untransformed measurement values.  We ran the three clustering approaches (PCA+HDBSCAN, UMAP+HDBSCAN, and original measurements+HDBSCAN) on a second dataset that includes more measurements (Antimony, Chromium, pH, Selenium, Arsenic, Cobalt, Potassium, Sodium, Magnesium) at the expense of not including two ponds (10172\_1 and 13114\_1). These ponds are missing data on the measurements in upgradient well for these other chemicals. In total, we explored 6 clustering approaches by combining the three clustering approaches with the two datasets.   |  | | --- | | Fig. 12: Fraction of clustering approaches recovering each pair of ponds in the same cluster. Two clusters can be defined based on the strong pond associations (>0.5) recovered: (1) 33108\_1, 10181\_1, 13114\_1; and (2) 22348\_12, 33446\_1, 33105\_1 (*plotted using notebooks/important\_notebooks/nb3\_upgradientPonds\_v3.ipynb*). |   This matrix shows the proportion of the explored clustering approaches that recovered each pair of ponds in the same cluster. By looking at associations recovered by more than half of the methods, we can be confident in defining two clusters, each including ponds located in sites that share a similar geochemistry:   * Cluster 1: 33108\_1, 10181\_1, 13114\_1 * Cluster 2: 22348\_12, 33446\_1, 33105\_1 |   See the following section for the potential association between local geochemistry of sites and boron level changes in the downgradient. |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
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# Impact of Pond Closure

Having explored upgradient information to find similarities between ponds that could be related to similar geochemistry between these sites, we next explored the information from downgradient wells to assess the impact pond closure has on groundwater quality. To measure the amount of boron that comes from the contaminated pond and not from the local geochemistry, we defined a metric named ‘relative boron concentration’, a measure subtracting the aggregated boron in the upgradient at each time point from its respective aggregated downgradient measurement at the same time point. Note that the closer this metric is to zero, the lower the release of boron from the pond to the downgradient water is.

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| Fig. 13: Difference in boron relative concentration between aggregated downgradient and upgradient wells for each pond every 4 months since closure construction started (*plotted with notebooks/important\_notebooks/nb4\_timeSeriesPlots.ipynb*).  From Fig. 13, we can see that closure in place ponds show much higher boron relative concentration values post-closure. This is however unlikely to be related to the closure method, since similar trends are observable before pond closure started (see Fig. 22 below). |

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| Fig. 14: Difference in relative boron concentrations between aggregated downgradient and upgradient wells for ponds with Closure in Place (CIP) every 4 months since closure construction started (*plotted with notebooks/important\_notebooks/nb4\_timeSeriesPlots.ipynb*). |

Restricting focus to ponds that were closed with the *closure in place* method, we can see that there are huge oscillations in the relative boron concentration over time, but the overall trend is a decrease, indicating that closure in place is reducing the release of chemicals from the pond.

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| --- |
| Fig. 15: Difference in relative boron concentrations between aggregated downgradient and upgradient wells for ponds with Closure by Removal (CBR) every 4 months since closure construction started (*plotted with notebooks/important\_notebooks/nb4\_timeSeriesPlots.ipynb*). |

If we now look at the trajectories for the *closure by removal* ponds (Fig 15), we can see that there are also huge oscillations in the data, in which we observe sudden decreases or increases of boron relative concentration values in short periods of time. We believe this is an artefact produced by how the well measurements are distributed over time in each pond (see the *Limitations With Sampling* section).

In order to capture global trends that could be masked by the heterogeneity in the data, and also to investigate changes that occurred prior to pond closure, we grouped the aggregated time-series data for each pond into four relative time bins. For each bin, we used the minimum value in relative boron concentrations recorded in each pond with comprehensive time-series information (Fig. 16). The four time bins were from first measurement to the laste waste deposit, from last waste deposit to closure start, from closure start to closure end, and from closure end to final measurement. It is worth noting that these time periods for individual ponds could be quite varied.

The trajectory of relative concentration changes over time display a clear decrease in CIP ponds after the first waste deposit until closure start, and also after closure start and closure completed. This analysis is limited however by boron sampling data only being available at each of the relative time-frames for 2 of the 6 CIP ponds.

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| Fig. 16: Minimum relative concentration values for boron registered for each pond over the four time bins shown. Only ponds for which information was available for at least the three time points were represented (*plotted with notebooks/important\_notebooks/nb4\_timeSeriesPlots.ipynb*). |

In contrast to the time-series trajectories of CIP ponds, the relative changes in boron concentration at CBR ponds do not show a clear trend. But there is a slight observable overall tendency to decrease over time, particularly after closure in place is commenced (Fig. 17). Some CBR ponds however undergo increases in relative boron concentrations over the time periods, particularly after closure started and closure complete, which may suggest that the process of closure is impacting local groundwater composition.

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| --- |
| Fig. 17: Minimum relative concentration values for boron registered for CBR ponds over the four time bins shown. Only ponds for which information was available for at least the three time points were represented (*plotted with notebooks/important\_notebooks/nb4\_timeSeriesPlots.ipynb*). |

Given the heterogeneous patterns that appear to be particularly prevalent for CBR ponds, we explored boron relative concentrations over time bins at a more detailed scale per pond, to investigate whether the timeframe-binning approach was removing more fine-grained detail (Fig. 18).

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| --- |
| Fig. 18: Relative change in boron concentration (mg/L) over time across all ponds with enough data. |

The visualisation above (Fig. 18) and other related plots are created by ‘Visualising Measurements Over Time.rmd’, in ‘important notebooks’. See Appendix: Rolling Median Plots of Each Measurement for more information on storage of all visualisations in the Box.

Overall, we can observe how ponds display large differences in trace patterns over the time scales sampled. As it is observable in Fig. 18, the time at which change-points in trace patterns occur often align with specific events, such as pond closure starting. Closure by removal can perturb in some cases the local geochemistry and lead to local increments in boron concentrations at the beginning of the closure event that later revert as seen for these ponds. The fact that we are detecting this pattern in some ponds (e.g., 22348\_2 and 33105\_1) exemplifies that our aggregation approach is appropriately capturing genuine signals from the data.

While the impact of these events tends to be pond-specific, interestingly, it appears that some of these tendencies may be driven by specific features of the local geochemistry. For example, ponds 22348\_2, 33446\_1 and 33105\_1, which were grouped in a same cluster based on background chemical levels (see *Similarities between sites* section), show anomalous increases of boron levels post closure completed. This highlights how local geochemistry may be connected to long-term compositional changes in groundwater composition and deserves further investigation.

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| --- |
| Fig. 19: Percentage change in boron concentration in downgradient data compared to the upgradient over time across all ponds with enough data. |

We proceeded to focus on one of the ponds displaying a striking increase in boron post-closure- 22348\_2- to investigate whether the rising boron levels were accompanied by increases in other measured groundwater chemicals. This is important as we are using boron to represent overall compositional changes. As can be observed in Figures 20 and 21, concentrations of many of the chemicals of interest at this pond peak at closure completion similar to boron. As with boron, several measured variables, including calcium, sulfate and chloride begin to accumulate again around 2021. However, this is not consistent across all chemicals, with the post-closure dip in concentration maintained for several metals found at lower concentrations, including arsenic.

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| Fig. 20: Percentage change in the first set of measurements between downgradient data compared to the upgradient data for Pond 22348\_2 which was treated with closure by removal (CBR) |

|  |
| --- |
| Fig. 21: Percentage change in the second set of measurements between downgradient data compared to the upgradient data for Pond 22348\_2 which was treated with closure by removal (CBR) |

Returning to aggregations at both the pond and time levels, we observe that there are overall similarities in the trajectories of change over time across ponds for the four best represented chemicals in our datasets: boron, sulfate, chloride and calcium (Figure 22).

To conclude, the end of the waste receiving period and the beginning and completion of pond closure significantly impact groundwater composition, with changes discernible across measured chemicals that occur at the same time as these events. Responses are highly pond and chemical specific, but we are able to capture several similarities. Pond closure is often associated with a spike in chemicals such as boron in groundwater composition, that generally then begins to decrease again. This is particularly observed for Closure by Removal ponds. A few of said ponds subsequently display increases in boron post-closure. We discover that several of these cases are linked by similarities in upgradient composition, highlighting how groundwater composition around ponds may impact post-closure fate. Finally, we observe that these findings are broadly common to other chemicals, further justifying boron as a representative for tracking groundwater composition.

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| Fig 22: Comparison of aggregated pond measurements for boron, sulfate, chloride and calcium across a range of binned time periods pre and post closure. (*plotted in differences\_relative\_timepoints.Rmd*) |

# 

# Cross-Well Comparisons

Whilst EPRI signalled to us that variations in boron were of most interest at the pond level (with data aggregated across wells at the same pond), focusing on what is occurring at individual wells still provides information of pond level behaviour. Therefore, we investigated post-closure trends at each well, and compared how the numbers of significantly changing wells varied at ponds of each closure method. Several methods were considered and attempted to determine changes post closure.

As is clear from Figures. 18 & 19, multiple post-closure behaviours, both monotonic and non-monotonic, are present and so should strictly be considered in any modelling. Thus, our first pass involved attempts at Multivariate Adaptive Regression Analysis (MARS) to create piecewise linear models from closure end dates. The rationale was that this should implicitly detect potential timepoints at which the gradient changes significantly. However, there was generally insufficient data, at least on a per-well basis, to accurately capture the varied changes observed so MARS tended to only locate one or two cutpoints. We also encountered similar issues with standard changepoint analysis based on changes in mean.

Therefore, we settled on a more traditional approach to detect trends: we ran a Mann-Kendall test on boron levels at each well from closure date to the most recent sample, and very roughly defined significance at p < 0.1. Accompanying linear models were used to determine the direction of this change. Two caveats should be mentioned here: firstly, Mann-Kendall tests for monotonic trends, which may be obfuscated by varied post-closure responses in boron levels, which sometimes begin increasing before levelling off again. Secondly, we did not perform multiple test corrections for the p-values produced. The justification for each of these issues is as follows: a) we were interested in whether we could determine a general trend, even when there were multiple turning points, and b) we were most interested in whether there were consistent changes in direction at wells, as opposed to specifically establishing significance (not least because the interest remains primarily at the pond level).

This approach determines that boron levels tend to lower rather than decrease at wells after pond closure, with boron decreasing at 44.9% and increasing at 8.99% of downgradient wells at p < 0.1. This difference is observed for stricter p-value cutoffs, and indicates a clear downward trend in boron post-pond closure (Table 5).

Table 5: Proportion of wells showing a statistical direction in change in measured boron readings after pond closure

| **Direction change in boron** | **Proportion of wells** | **Raw P-value cutoff** |
| --- | --- | --- |
| Up | 8.99 | 1.00E-01 |
| Down | 44.94 | 1.00E-01 |
| Up | 2.25 | 1.00E-02 |
| Down | 24.72 | 1.00E-02 |
| Up | 1.12 | 1.00E-03 |
| Down | 16.86 | 1.00E-03 |
| Up | 0.00 | 1.00E-04 |
| Down | 14.61 | 1.00E-04 |

The proportion of downgradient wells with post-closure changing boron levels is clearly distinguishable from upgradient wells, validating the approach (Table 6). Differences between up- and down-gradient trends are more stark at stricter p-value cutoffs.

Table 6: Proportions of upgradient vs. downgradient wells with significant changes in boron concentration post-pond closure

| **Well gradient** | **Proportion of wells with significant post-closure boron trends** | **Raw P-value cutoff** |
| --- | --- | --- |
| Downgradient | 53.93 | 1.00E-01 |
| Upgradient | 32.84 | 1.00E-01 |
| Downgradient | 26.97 | 1.00E-02 |
| Upgradient | 7.46 | 1.00E-02 |
| Downgradient | 17.98 | 1.00E-03 |
| Upgradient | 1.49 | 1.00E-03 |
| Downgradient | 14.61 | 1.00E-04 |
| Upgradient | 1.49 | 1.00E-04 |

We next divided wells based on the removal method of their associated ponds. Here, we observe that Closure in Place ponds are typified by both a greater proportion of wells displaying decreases in boron levels (Fisher’s test: p = 0.0018) and a lower proportion of wells with increases in boron post pond closure than for Closure by Removal ponds (p = 0.0068). This is also clearly visible on a per-pond level (Figure 23).

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| Fig. 23: Differences in numbers of wells displaying post-pond closure increases in boron at CIP and CBR ponds. Left) Collating wells across all ponds, a higher proportion of CIP-pond associated wells hae decreasing boron levels, and a slightly lower proportion increasing boron levels. Right) This is also observable at the per-pond level *(Plotted from well\_trends.Rmd).* |

Notably, several of the previously highlighted ponds display both post-closure increases in boron and clustering together based on HDBSCAN on upgradient groundwater compositions (22348\_2, 33446\_1 and 33105\_1) have relatively high numbers of increasing, and fewer decreasing wells. Apparent differences between CIP and CBR ponds may therefore be due to each pond in this cluster being closed by removal. As this could bias analysis, we removed these ponds from the CBR vs CIP analysis, demonstrating that this does not abolish the lesser incidences of CBR wells displaying reductions in boron post-closure. However, the higher incidences of wells with increasing boron levels post-closure at CBR ponds are reduced, so this finding is likely caused by this subset of ponds (Figure 24). This highlights the need for caution in drawing conclusions from differences in a complex dataset based on only 18 ponds.

On the other hand, using an imperfect approach (multiple Mann-Kendall tests on complex-structured trends), we could find statistically significant differences in the impact of Closure by Removal and Closure in Place. It also demonstrates the usefulness of considering trends across wells at a pond, alongside aggregating all data to a pond level. One final caveat of this analysis is that it does not consider time points prior to closure. Therefore trends in boron concentration that began before pond closure would complicate the impact of CBR vs. CIP closure analysis. It would be prudent to repeat this analysis, specifically classifying trends that occur upon closure starting on being completed, rather than just using closure completion as a starting point.

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| --- |
| Fig. 24: Removal of wells for a cluster of ponds where increasing post-closure boron may be due to local geochemistry. Discounting ponds 22348\_1, 22348\_2, 33105\_1 and 33446\_1 from analysis impacts the difference in the proportion of wells with increasing boron levels post closure for CBR vs. CIP. However differences in wells with reduced boron are maintained. |

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# Future work

Much of the task in this project was dedicated to processing the available data into a form appropriate for cross-pond comparisons. With this accomplished, there is now increased scope for further analysis. One clear area of future analysis is to continue tracking data. For the majority of ponds closure was only completed within the last 5 years (5/18 ponds), as outlined in Figure 4. We have outlined several ponds at which boron levels are currently rising in the surrounding wells post-closure; whether this trend continues or levels off should become clear as samples continue to be taken.

Similarly, we have generally focused on trends in boron concentrations across time. At several places in this report, we have highlighted how this relates to the fate of other chemicals comprising local groundwater (e.g. Figures 20-22). However, this has mostly been confined to visual analysis. A possible next step would be to expand this to multivariate analysis. Something along the lines of MARS (multivariate adaptive regression splines) may be of particular interest, as this would allow for modelling without making assumptions on trends, which are highly variable between ponds and chemicals.

MARS would have benefits over the linear modelling and use of a Mann-Kendall test, as it would better deal with non-monotonic traces. It would also allow for better determination of whether initial increases in boron post-closure are consistent or continue to vary. Whilst it was not the most appropriate method to use in the short term case of the few years post closure, it should be more robust over the entire time-courses considered, and at the aggregated pond level. Further, this kind of modelling will be more feasible in the post-closure context as further samples are collected.

Across the entire time course, analysis such as MARS would also allow for the classification of how different events (the end of waste receival or pond closure) are associated with change points in trends, especially for determining whether such changes are consistently occurring across different variables.

On a chemical-by-chemical level, an alternative approach to this would be to use peak-calling or inflection point analysis to calculate the distances between peaks or increases/decreases to closure dates. This could be compared to expected distances using a permutation strategy, which could be used as a non-parametric statistical test to confirm that changes in downgrading groundwater composition align with these events. Similar analysis on individual wells could also be used to distinguish upgradient wells that are being impacted by closure (which may affect other analyses) or downgradient wells that are not affected by the pond despite their downstream positioning, as trending at these wells should be random.

Comparisons of the distributions of peak prominences around specific events could be used to determine whether perturbations in local groundwater are more associated with the end of waste depositing compared to closure, or as another approach to determine the significance of the differences between CIP and CBR. It would also provide a means to answer questions regarding how immediate changes in groundwater composition occur post-closure, and how different chemicals act differently. This could accompany or replace the linear model/ Mann-Kendall test in the well level analysis.

On a separate track, we detected an association between a group of ponds that display increases in boron post-closure and that also cluster based on similarities in upgradient boron, sulfate, calcium and chloride concentrations. This association hints at a potential link between local groundwater composition and the resultant impacts of pond closure. But we did not ascertain \*how\* factors contribute to this. A next step would be to explore how this cluster of ponds differs from other ponds by groundwater composition, and to determine whether there are any clear reasons why this may be impacting long-term groundwater boron trends. Analysis could also be expanded to consider other factors, such as ORP, dissolved oxygen, temperature and pH that may be expected to influence trends.

# Appendix

## Rolling Median Plots of Each Measurement

These plots will be submitted in PDF form, contained within the Box folder provided by EPRI. They will be stored in ‘Appendix/Figures/Rolling Median/’ as either ‘nominal’ or ‘proportionate’ referring to plots in relevant units or percentage change from upgradient respectively. ‘Ponds\_scatter’ plots will show all ponds for the measurement named in the filename. Files beginning with a pond ID number will either contain measurements of interest or chemicals of environmental concern dependent on filename.

Note, if plots are empty or missing from these files, it is because the dataset does not contain values for these ponds/measurements. Cleaning was done to reduce this effect on the outputs but it has not been automated in its entirety.

These plots are produced by ‘Visualising Measurements Over Time.rmd’, which can be run to regenerate these plots, or edited to change parameters of the visualisation.