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AN ANALYSIS OF GROUNDWATER QUALITY AS SAMPLING NETWORKS AGE: THE GAPS IN GROUNDWATER MONITORING

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Submitted in partial fulfillment of the requirements for graduation with Distinction

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Abstract

Groundwater management is an important facet of protecting this important resource. One way that we ensure proper groundwater management is through the regular, long-term monitoring of groundwater wells at waste management sites throughout the country. This study investigates potential changes to groundwater quality attributed to degradation of well construction materials rather than impacts to aquifers from wastes. This assessment was completed using a data analysis of groundwater trends at closed landfill sites. An analysis of fifty-five sites was completed and three sites met our criteria for suitable data history. Due to the lack of suitable data, a more thorough investigation is needed to determine if changes in groundwater quality can be attributed to degradation of well construction materials.

Acknowledgements

First off, I must express my sincere appreciation and thanks to my advisor and professor Dr. Kevin Svitana. I have been in at least one of Dr. Svitana's classes every year since my freshman year and it has been a pleasure to learn under his direction and have his support through the past two years of developing this project. I also am incredibly grateful to Dr. Lehman and Dr. Burk for being members of my Distinction Committee and their flexibility throughout this period of time. To Dr. Bouchard, thank you for pushing us to better our writing and understanding of research in Senior Seminar this Spring. Your support has been unwavering.

Thank you to the Ohio Environmental Protection Agency for providing us with the data to be used in this project. Specific thanks goes to Mike Slattery and Katie Rader for their time and help in identifying and sorting the data that made this all possible.

Another huge thank you to Greg Shipley whom I work with at Math Plus Academy. He created a program which processed the data and filtered it down to the parameters we were looking for. Without his help, I'm sure this would have taken an immensely larger amount of time and for that I will be forever grateful.

Thank you to Alyssa Fogel for supporting me in school and always offering to edit things for me. You are going to be an amazing Environmental Scientist.

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Last but of course not least, thank you to my parents for listening to me say, "Sorry, I can't. I need to work on my thesis" way too many times in the past year. I love you both and can't express how thankful I am for your help to get this wonderful education. See you soon.

Introduction

Groundwater management is an important facet of environmental sustainability. One way that we ensure proper groundwater management is through the regular monitoring of wells at sites throughout the country. This study investigates potential changes to groundwater quality attributed to degradation of well construction materials over time by completing a data analysis of groundwater trends at closed landfill sites. Issues may arise if the cause of an increase in compound and analyte concentrations is related to well deterioration, not from wastes. Data analysis of existing Ohio Environmental Protection Agency data bases on compounds and analytes such as iron, chromium, sulfur, chloride, sodium and plastic byproducts will be used for this study. Selected sites will include sites with multiple types of well constructions to determine if well deterioration, not waste mobilization, is the cause of an increase in said compound and analyte concentrations. If it is found that compounds and analytes have an upward trend over these longer periods of time, it may affect the compliance and economic projections of the closed sites. If upward trends are from well construction material deterioration rather than from waste, unnecessary additional assessments would be required. One example of this may be that those responsible for landfill management may be forced to complete additional assessment to determine if the changes in groundwater quality are related to migration of waste leachate when the changes are related to changing well conditions, not the mobilization of waste.

Often, indicator compounds such as the ones listed above are used as indicators of groundwater quality change related to waste leaching because of their mobility in aqueous solutions. This study intends to determine if well deterioration is a source of these indicator compounds.

When a hazardous waste management unit stops receiving waste at the end of its active life, groundwater monitoring continues to demonstrate waste containment is being maintained in accordance with the Resource Conservation and Recovery Act (RCRA) protocols. This is called post-closure care. Post-closure care is required for land disposal units that leave waste in place upon closure such as landfills, land treatment units, surface impoundments, or any other hazardous waste management that cannot achieve clean closure standards. These sites must monitor and maintain liners, final covers, leachate collection and removal systems, leak detection systems, and gas collection systems to protect the surrounding environment and population from releases of hazardous constituents. The standard post-closure care is thirty years ("Closure and post-closure care requirements for hazardous waste treatment, storage and disposal facilities," n.d.).

Because the earliest closed hazardous sites are now reaching the end of their standard thirty-year post-closure monitoring phase, little research has been done to determine if upward concentration trends in compounds and analytes in groundwater samples attributed to monitoring well construction material degradation occurs. When sites start remediation at the beginning of the post-closure period, sampling occurs quarterly for a minimum of two years in order to establish a baseline of groundwater quality. This typically continues for at least five years before it can revert to semiannual or annual. Now closed waste sites are reaching their thirty year postclosure anniversary, requirements to sample are reduced to as little as once every three years which may lead to a higher prevalence of compounds and analytes that are due to well deterioration and based on well construction, not the mobilization of contaminants from the waste source, in the groundwater samples.

Groundwater is water found underground in the cracks and spaces in soil, sand and rock. It is stored in and moves slowly through geologic formations of soil, sand and rocks called aquifers. Aquifers represent an important water resource as water within aquifers and groundwater supplies drinking water for 51% of the total U.S. population and 99% of the rural population ("What is groundwater," n.d.). When groundwater testing occurs, samples are taken from groundwater monitoring wells at the site. Sampling methods vary from site to site and are dependent on site-specific conditions and requirements in addition to data-quality objectives and well accessibility. However, for each sample, to prevent collecting a sample of stagnant water which may not represent true water quality, the well must be purged prior to sampling. Additionally, a poor sample can result from over-pumping of the monitoring well. This could dilute contaminant concentrations which would not represent the true water quality. After samples are collected, they are then analyzed for parameters such as arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, sodium, mercury, and chloride. (Yeskis & Zavala, 2015).

The wells that are used to obtain groundwater samples are made of different materials such as steel, stainless steel, PVC, and Teflon[™]. When these wells deteriorate over time, there is a risk of releasing iron, chromium, sulfur, chloride, sodium and plastic byproducts. These will be the compounds and analytes will be the focus of the data set.

We chose to complete this study because water is a valuable resource. One writer for the Los Angeles Times, Peter Engelke, explains that when water is present and accessible, it is an enabler of good things. It is beneficial to human health, food production, energy production, to name a few. However, when we lack access to a sufficient water supply, human health and the environment suffer, among other things (Engelke, 2016).

Most sites are now reaching the end of their thirty-year period and forever monitoring is looming ahead. Therefore, this is a portion of groundwater monitoring and management that hasn't been studied yet. If it is found that compounds and analytes related to well deterioration have an upward trend over these longer periods of time, it will affect the compliance criteria and economics of the closed sites. If the cause is not from waste, then other issues come into play as it would be expected that upward trends are from waste. One example of this may be that those responsible for cleanup may be forced to complete additional assessment because of groundwater quality. However, the groundwater change is related to changing well conditions, not the mobilization of waste

Methodology

In order to determine the changes in groundwater quality as sampling networks age, we decided to complete an analysis of data maintained by the Ohio Environmental Protection Agency (OEPA). This included historical data at monitored sites such as landfills and superfund sites dating back to 1980.

In July of 2019, I reached out to the OEPA in order to obtain site data. On September 5th, Dr. Kevin Svitana and I met with a group of OEPA members to discuss the scope of our project. They supplied us with an Excel spreadsheet of fifty-five sites that have been monitored historically and that also matched the parameters we were looking for such as concentrations of dissolved arsenic, dissolved calcium, dissolved iron, sulfate, chloride, arsenic, calcium, and iron.

From the list of fifty-five sites received, twenty-five were selected that contained data for at least eighteen years (1985-2003) and at most thirty-seven years (1981-2018). All data analyzed in this stage began being collected at minimum prior to 1990 which was considered long enough to show a possible statistical trend. The other thirty sites were deemed to not have enough data to be statistically relevant. From the twenty-five sites selected to be analyzed, data was sorted by our parameters including dissolved arsenic, dissolved calcium, dissolved iron, sulfate, chloride, arsenic, calcium, and iron. There were multiple wells for each site where data was collected, so data for each parameter at each well at each site was used to visualize the data. The data for these parameters was used to create graphs in Excel to show the change in each parameter concentration in each well as a function of time.

Out of the twenty-five total sites analyzed, three sites contained data with more than eight sampling dates: Solvay AMACO, USS Kobe Steel, and Vickery Environmental. Eight samples is the OEPA minimum to investigate statistical trends, so that is the minimum we used, as well.

Once graphs were completed, we looked to focus on sites and wells that had upward trends in the parameters we were investigating. This allowed us to begin to attempt to determine if certain types of well construction are more susceptible to deterioration over time and what the extent of that deterioration may be based on the concentrations of compounds and analytes present in their samples.

Results

The results of our study revealed one key finding: there is not enough data to reach a conclusion regarding the deterioration of wells impacting groundwater quality.

The final number of wells that had eight or more data points was 120 and 63 of those had an upward trend (a positive slope in the trendline). Therefore, 52.5% of the total wells meeting the requirements to be statistically analyzed had an upward trend while 47.5% had a downward trend in analytes over time.

Of the 63 that had an upward trend, Sulfate was the highest counted at 21 wells followed by Dissolved Arsenic with 13, Chloride with 12, Arsenic with 9, Dissolved Calcium with 7 and Calcium with 1.

Additionally, these wells only represented three sites (Solvay, USS Kobe, and Vickery) out of the fifty-five original potential sites and the twenty-five we focused on with historical data we deemed applicable. Because of this, we are unable to look at a good representation of various site geology and well construction.

Vickery Environmental is located in Vickery, Ohio at 3956 OH-412 Vickery, OH 43464 (Figure A2). The wells at Vickery are primarily constructed out of Stainless Steel and Plastic ("Water well log and drilling report, n.d.). The geology of the site falls in the Silurian age in the Ice-Scoured Bedrock Landscape area of Ohio. The Silurian age in this area means the geology is primarily dolomite, medium to massive bedded ("Geologic units in Sandusky county, Ohio, n.d.). In dolomite, groundwater mainly occurs in fractures. ("Shaded bedrock-topography map of Ohio, n.d.)

USS Kobe (also known as Republic Steel) is located in Lorain, Ohio at 1807 E 28th St Lorain, OH 44055 (Figure A3) and primarily has PVC Slotted wells. The geology in Lorain is Devonian age and primarily consists of a sandstone aquifer ("Shaded bedrock-topography map of Ohio, n.d.).

Solvay also has PVC slotted wells and is located in Marietta, Ohio at 17005 OH-7 Marietta, OH 45750 (Figure A4). The geology in Marietta is Permian-Pennsylvanian age and is primarily a sandstone/shale, sand, and gravel mix ("Shaded bedrock-topography map of Ohio, n.d.).

The lack of sites with substantial data meant we were unable to use geology or well construction to find a correlation, however there are still interesting trends that could be examined more closely.

In Appendix B: Sulfate Trend Graphs, concentrations in Figure B1 decreased overall from February 2008 to March 2012 and have been increasing overall since then. Figure B2 concentrations decreased from August 1999 to August 2004 and have also been increasing steadily from August 2004 to the last recorded date in February 2011. Figure B3 has an overall increasing trend from February 1998 to February 2009 and then a sudden spike in concentration from February 2009 to the last recorded date in February 2011. Figure B4 has less data points but still shows an increasing trend overall. The biggest increase was from September 1986 to March 1987 where concentrations went from about 95 mg/l to about 140 mg/l. There was a slight decrease through the end of 1987. Figure B5 has had a steady increase from February 1996 to February 1997 when there was a spike through March 1998. This spike was from about 5 mg/l to

25 mg/l. Figure B6 has increased steadily from November 1998 to the last recorded date in January 2008.

In Appendix C: Chloride Trend Graphs, concentrations in Figure C1 had two spikes of about 350 mg/l: one around June 1996 and one in June 1998. Figure C2 has relatively steady increase over time with a spike of about 60 mg/l from June to August 1998.

In Appendix D: Dissolved Calcium Trend Graphs, concentrations in Figure D1 fluctuate before increasing steadily from May 1997 to the last recorded date in May 1998.

Each graph shows a trendline with equation and an r-squared value. The r-squared value is a statistical measure of how close the data is to the trendline. The higher r-squared values represent a stronger lean towards a consistent trend.

Discussion

There is large variance in the data over time. Some parameters saw a decrease before seeing a steady increase in their later testing dates; These provide a bit more interest and may suggest our hypothesis could be supported.

As previously mentioned, groundwater is an important resource. As the population increases, our need to sustainably manage groundwater will only continue to increase, as well. This sustainable management includes proper monitoring and remediation techniques. It has become obvious that there is a lack of good databases to monitor our groundwater all in one place. The OEPA is working to create these databases, but there is still work to be done.

Another organization, the International Groundwater Resources Assessment Centre (IGRAC), completed a report titled "World-wide inventory on groundwater monitoring". The inventory was completed 2003-2006. It included a questionnaire on groundwater monitoring which was sent to 233 countries, studies on reports of international organizations with respect to monitoring, conducting internet searches for documents on groundwater monitoring, and interviewing experts from international water projects among other tasks.

The questionnaire included four subject areas: The groundwater situation in the country, the quantity of groundwater monitoring, the quality of groundwater monitoring, and the technical support required from IGRAC. The study received answers from 44 people in 40 countries. Only three of these were in North America. The one in the United States was the United States Geological Survey.

Historically, the groundwater observation well network was nationwide by the end of 1960. The United States did have an integrated management system at the time of this study

meaning we were considered pro-active in managing groundwater (Jousma & Roelofsen, p.11) and had a national or regional reference groundwater monitoring network operation in combination with local groundwater monitoring networks (p.8). However, the opinions of respondents on the density of observation wells in the United States was that it is insufficient. (p.14). Frequency of observation of groundwater level was rated as good (p. 17). For groundwater quality monitoring, there is only a background monitoring network for groundwater quality characterization in large regional aquifers (p. 23).

Though the study did not focus on database management, it does highlight the need for better record management and monitoring in the future to ensure a sustainable and healthy groundwater supply. We must continue to be proactive in our groundwater management.

In order to improve the results of this study, a larger sample size would be beneficial as it would increase the likelihood of obtaining sites with different well construction and geology which could have an impact on upward trends in constituents. Our samples are all located in Ohio so one option may be to expand the number of states investigated or look nationally. Some states may have larger networks and records which could also be beneficial. There are likely other databases that would be able to supply additional information, as well. Even the data obtained from the Ohio EPA was not complete for this study as they are currently working to get data into online databases, so as time continues additional databases may be completed.

Additionally, more testing at each location already investigated is important. Many of the sites that we saw increases or spikes have not been tested since 2008 as the most recent sample date. Have the concentrations continued to increase in the last twelve years, or have they decreased to a stable concentration again? We do not know what has happened with the

groundwater quality since then and thus our hypothesis that well deterioration is causing an increase in constituents could still be possible.

Not limiting the time frame of data to be researched would have also allowed for a larger sample size. Because we selected sites that only had data prior to 1990, that could have reduced any sites that have more recent data even if it was not as long of a time period.

Additionally, for future study, it would be interesting to investigate why Sulfate appeared to have the highest number of upward trends. Is this consistent across additional sites and databases? What could be the cause of specifically Sulfate increasing over time? Obtaining more data points would also allow us to look more at whether different well constructions is what is causing potential trends or if it may be different bedrock types. Unfortunately, it all comes down to the need for a larger, more recent data set.

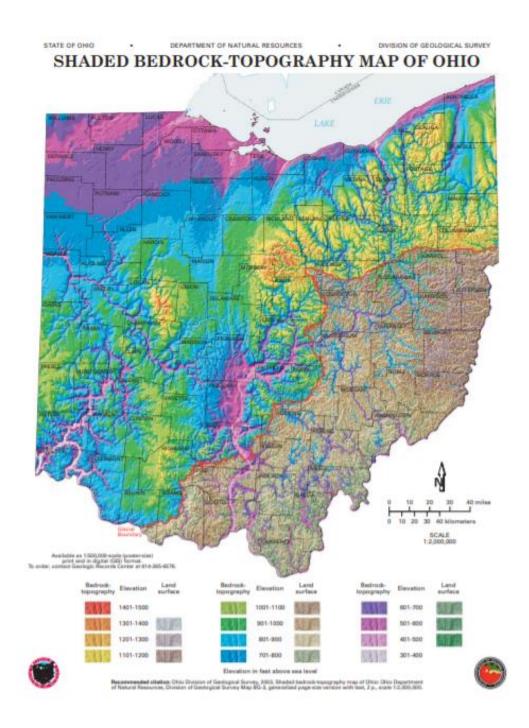


Figure A1. Map obtained from the Ohio Department of Natural Resources Division of Geological Survey which depicts bedrock-topography across Ohio.

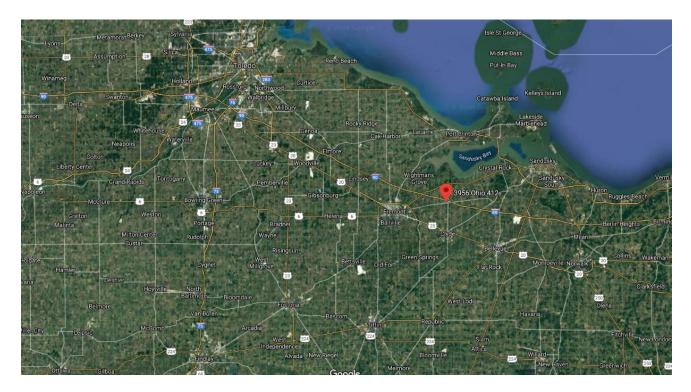


Figure A2. Location of Vickery Environmental at 3956 OH-412 Vickery, OH 43464.

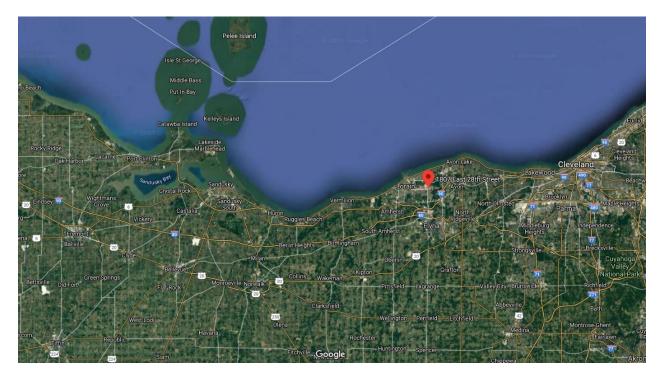


Figure A3. Location of USS Kobe Steel at 1807 E 28th St Lorain, OH 44055.

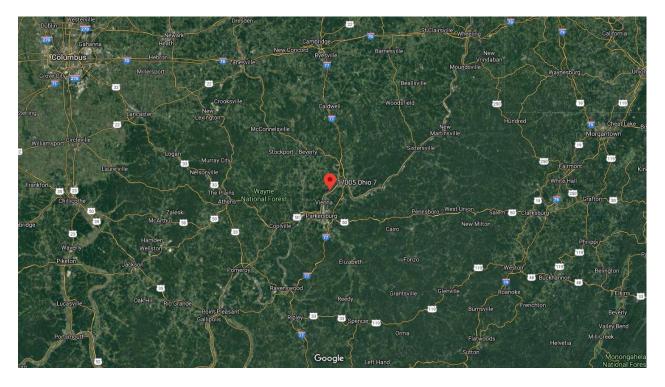
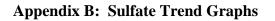


Figure A4. Location of Solvay at 17005 OH-7 Marietta, OH 45750



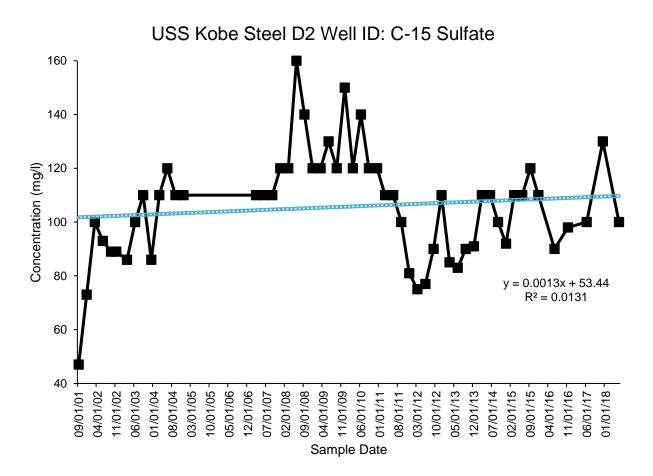


Figure B1. Concentration (mg/l) of Sulfate over time at USS Kobe Steel Well ID C-15. Each point represents a sample taken from the well and analyzed.

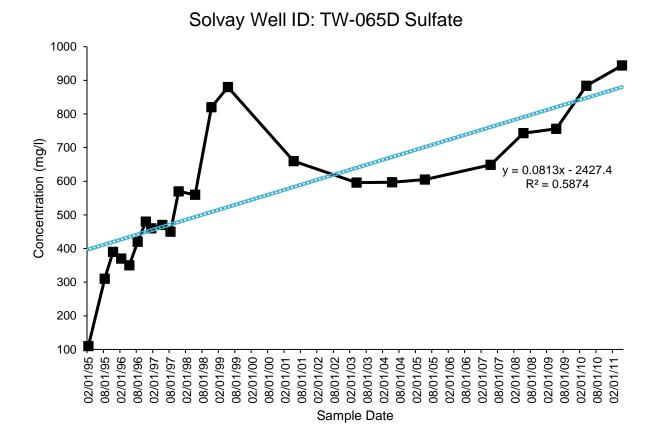
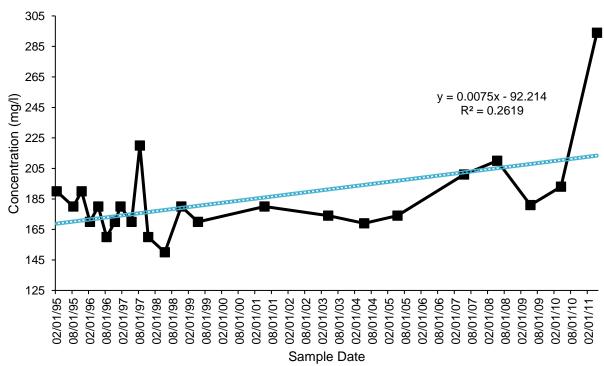


Figure B2. Concentration (mg/l) of Sulfate over time at Solvay Well ID TW-065D. Each point represents a sample taken from the well and analyzed.



Solvay Well ID: TW-057S Sulfate

Figure B3. Concentration (mg/l) of Sulfate over time at Solvay Well ID TW-057S. Each point represents a sample taken from the well and analyzed.

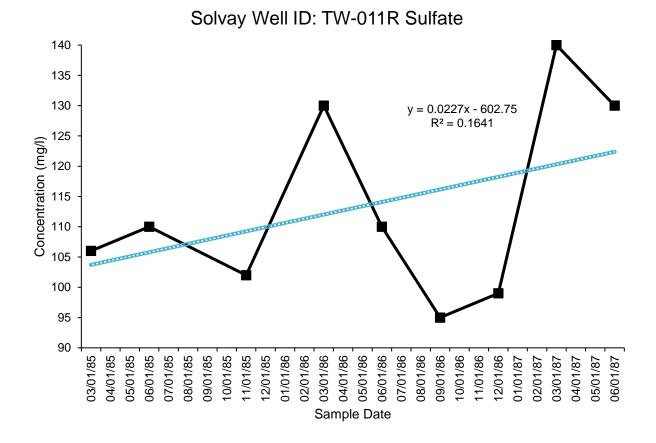


Figure B4. Concentration (mg/l) of Sulfate over time at Solvay Well ID TW-011R. Each point represents a sample taken from the well and analyzed.

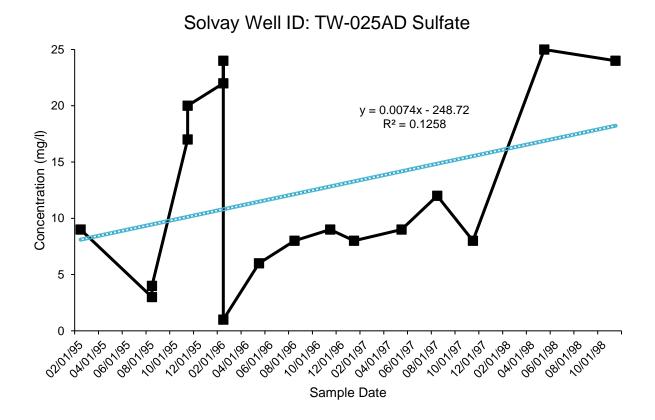


Figure B5. Concentration (mg/l) of Sulfate over time at Solvay Well ID TW-025AD. Each point represents a sample taken from the well and analyzed.

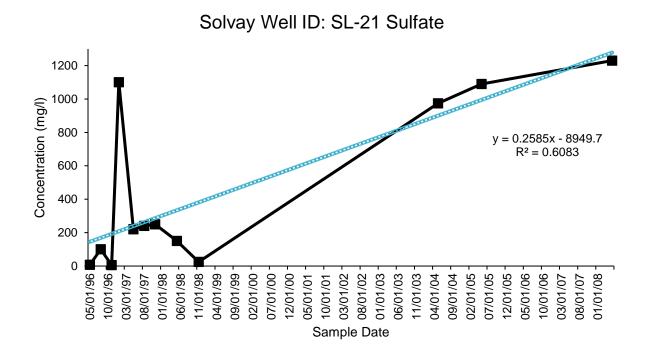


Figure B6. Concentration (mg/l) of Sulfate over time at Solvay Well ID SL-21. Each point represents a sample taken from the well and analyzed.

Appendix C: Chloride Trend Graphs

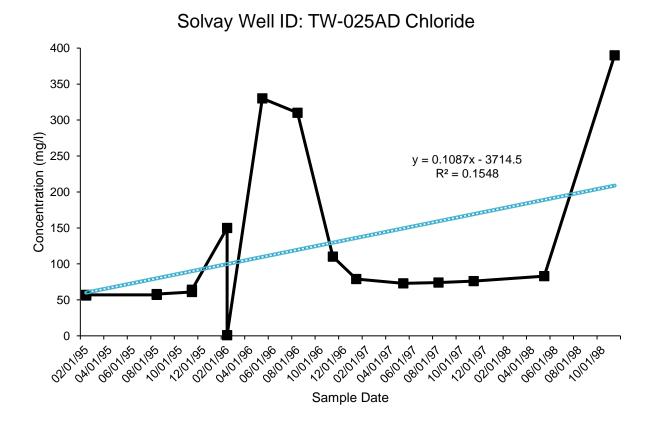


Figure C1. Concentration (mg/l) of Chloride over time at Solvay Well ID TW-025AD. Each point represents a sample taken from the well and analyzed.

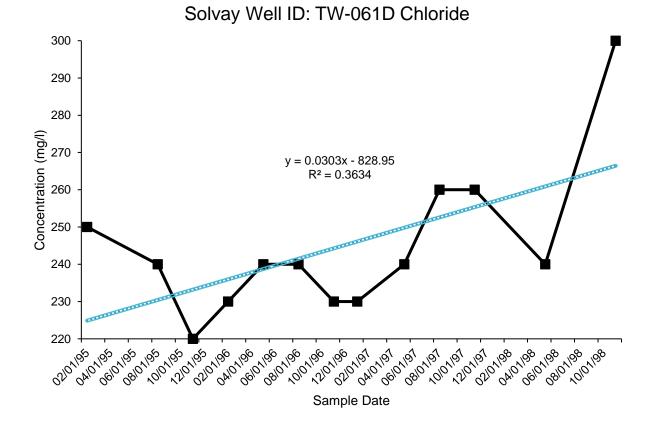


Figure C2. Concentration (mg/l) of Chloride over time at Solvay Well ID TW-061D. Each point represents a sample taken from the well and analyzed.

Appendix D: Dissolved Calcium Trend Graphs

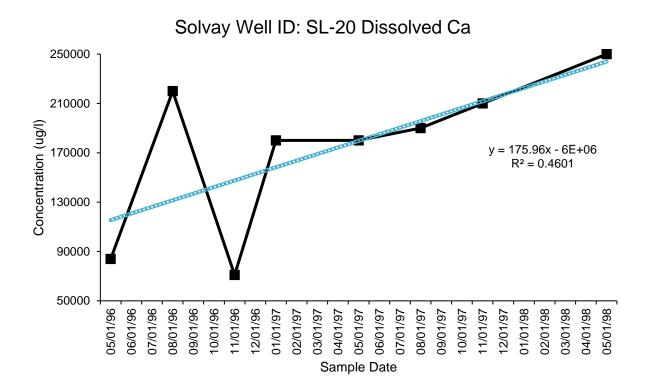


Figure D1. Concentration (mg/l) of Dissolved Clacium over time at Solvay Well ID SL-20. Each point represents a sample taken from the well and analyzed.

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