Trends in Concentrations of Inorganics at Norske Skog Tasman Pulp and Paper Mill Solid Waste Site

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Abstract:

This report investigates the spatial and temporal trends of contaminants produced by the Norske Skog Tasman Pulp and Paper Mill, and disposed at former Lake Rotoitipaku, Kawerau, New Zealand. Water samples were collected from a spring source and two on site water bodies, in addition to soil samples taken along transects running through the waste site. The soil samples were used to create leachate, which was tested with the water samples for anions (sulfate, nitrate, chloride, phosphate) and cations (Na, Mg, Ca, K). The experiment found trends in the data suggesting elevated contaminants at various levels due to age of the contaminant, spatial distribution, and chemical properties. This provides valuable information on the extent of contamination in the site and surrounding areas, which helps guide correct environmental responses.

Introduction

Contamination of local soils and water bodies have far reaching impacts on communities and ecosystems outside of the immediate area. Contaminants can seep into the ground water or carried into rivers, where the pollutants can be transported over many kilometers and damage countless systems. Many operational sites for waste disposal have been in use for decades. These sites commonly are not suitable for handling the waste and have been poorly monitored over years. Consequently, this could lead to the degradation of the land, loss of biodiversity, and destruction of aesthetic qualities and other ecosystem services beneficial to humanity.

Paper mills are notorious for producing a wide range of toxic wastes. These include NaOH, HCl, H2SO4, Pb, CN, H2O2, Cl, PCBs, dioxins, waste sludge, VOCs and phenols (Howell 2011). There have been reports of paper mills all over the world causing considerable pollution to rivers, wetlands and other environments (Devi 2010). Studies have proven direct correlations between drastic environmental damage due to

contamination and the proximity of pulp and paper mills (Paukan 2003). Organic contaminants are notorious for their extremely detrimental effects, but in most cases the wastes have been predominantly inorganic. This varies mostly on production type. Inorganics tend to prevail in printing paper sludge, while higher concentrations of organics are in packing paper sludge (Zule 2007). Tasman Mill produces newsprint.

The Tasman Mill deposits treated waste on a site adjacent to the Tarawera River, previously the location of Lake Rotoitipaku. Although the waste is considered treated, the extent of the contamination to the surrounding area is understudied. Waste considered safe for disposal can leach ions and heavy metals into the groundwater and surface water and older studies have found evidence of the pollution of the immediate area, Tarawera River, and habitats downstream (Wilkins 1997, 1998; Watching 1981).

This study focused on the spatial trends of inorganic contaminants leaching into the soils of the Tasman landfill. The hypothesis expected a positive correlation between the level of contamination in the leachate, and the sample location relative to the center of the waste site. This study used a variation of Howell's successful method based off of the EPA's Toxicity Characteristic Leaching Procedure, or TPLC (Howell 2011; Davis 2001). Leachate was analyzed for cations and anions using a High Pressure Ion Chromatography (HPIC) and Atomic Absorption Spectroscopy (AAS). With this data, it was be possible to assess trends hinting to the extent and range of harm the waste site could have on the surrounding area.

Background

The Norske Skog Tasman Pulp and Paper Mill is located on the outskirts

Kawerau, a town in the Rangitaiki Plains, Bay of Plenty, New Zealand. It is powered by a 100-megawatt geothermal power plant fed by the nearby Mt. Putauaki. The mill is the largest single employer in the region, and along with three other paper mills in the area it makes up over $1 billion of New Zealand's GDP (FA course book 2012; Howell 2011). This gives Tasman significant political and economic influence. Up until 1964, the Tarawera River was the mill's primary waste disposal site. Due to extreme contamination effects on the river, the government enacted the Tasman Act, which gave the company freedom to designate a location for waste disposal. In 1971, Lake Rotoitipaku became Tasman's solid waste disposal site (Hikuroa 2011).

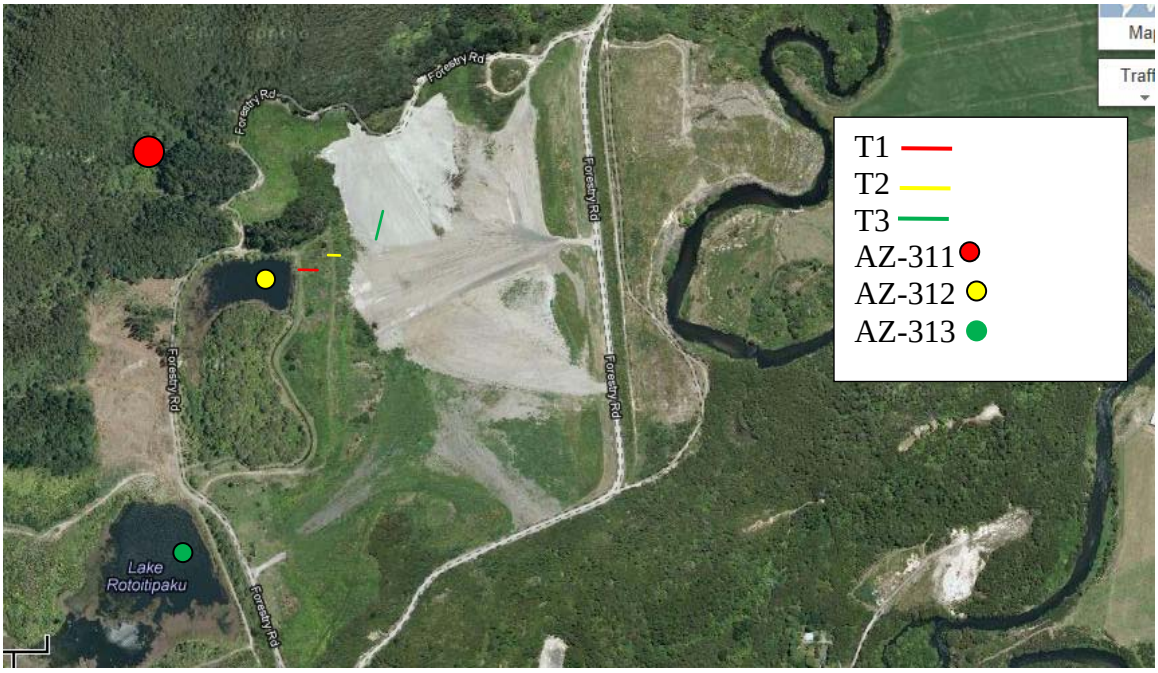

Figure 1 – *Site Map: Lake Rotoitipaku Solid Waste Landfill*

Prior to 1971, Lake Rotoitipaku was a scenic shallow water lake. The land was spotted with geothermal pools and sinter terraces. The area was of great cultural, spiritual, and economic importance to the local Iwi tribe. The lake provided a vital food source, medicinal properties, and a place of community gathering. Rotoitipaku was fed

by a fresh water spring considered to be sacred (Hikuroa 2011).

Currently, Lake Rotoitipaku is buried under more than 20 meters of waste. The geology of the area was not taken into consideration when the site was designated for waste disposal. The 600,000 cubic meters of waste is sitting on top of a faulted, permeable, unconsolidated material, and active geothermal location. The waste site is roughly 30m above the nearby Tarawera River, and is believed to have a very high water table. The only barrier between the river and waste site is a non-engineered embankment that had failed three times in the 1980s, releasing large amounts toxins into the river. The local groundwater fails to meet drinking water standards, and the soil exceeds international standards for several contaminants such as dioxins, mercury and arsenic (Borella 2007, Hikuroa 2011).

Globally 70-74% of paper mill solid was has been discarded in landfill sites (Zule 2007). According to the Norske Skog annual report released in 2009, the waste production of the paper mill consists of 399,000 tons of sludge, 138,000 tons of bark and 45,000 tons of other materials (Norske 2009). Most paper mills have a primary and secondary waste treatment process. In primary treatment, much of the larger material is removed and recycled back into the paper production, and the smaller suspended material produces sludge that is moved to secondary treatment. The purpose of the secondary treatment is to reduce the biochemical oxygen demand (BOD). BOD is the amount of dissolved oxygen required for aerobic organisms to break down organic material in water. Lowering BOD would allow the harmful organics to break down quickly and more easily. However, this does not affect the inorganics. After secondary treatment, the sludge is then moved to a dewatering process. This is done to minimize the volume of

the solid waste. The water from this process is then further treated, and the solid waste is disposed of in a landfill. Sometimes the solid waste is burned prior to disposal (Amberg 1984).

The Rotoitipaku waste site is subject climate conditions. As a result, there is significant exposure to rainfall, which infiltrates the soil and causes leachate to flow through the permeable, underlying rock into the groundwater system (Hikuroa 2011). Inorganic contaminants, such as Na, have an extremely negative impact on soil quality. Na can increase sodicity and destabilize the soil (Patterson 2008). High concentrations of ions, such as Ca, Mg and Na, can adversely affect soil permeability and reduce the rate of water intake. Na also can act as a deflocculating agent, and cause the soil to cumulatively lose productivity by displacing divalent cations like Ca and Mg (Phukan 2003). The decreased infiltration could result in more contaminated runoff going into the Tarawera River. Despite low levels of soil infiltration, the toxins have been around so long they have most likely made it into the groundwater system. Over the decades of contamination, the soil has become less and less likely to recover.

Methods

The samples were collected in the field between the hours of 12 and 1pm on February 10th, 2012. It was a sunny day, and the surface soil was dry when not near the ponds. Soil samples were collected from three transects, T1, T2, T3 – see *Figure 1 Site Map*. Along each transect, ~100g of soil sample was collected every two meters. The first transect began at the larger water body. Twelve samples were collected at two meter intervals and marked as T1-S1; T1-S2; T1-Sn… ect – Sn stands for the sample number

along the transect. Transect 2 was collected at the vegetation line and across a dirt road about 10m from Transect 1 towards the waste site. Only three samples were collected along this transect – T2-S1; T2-S2; T2-S3. The final soil samples were collected along the third transect ~50m into the exposed sediment and solid waste material, and was directed further into the waste site. Six samples were collected along Transect 3 starting with T3-S4 and ending in T3-S9. The transect locations were not well marked in the field notes. Figure 1. illustrates the approximate location of the transects and sampled water bodies.

The water samples were collected at three points. Two were collected from ponds on the edges of the waste site and a third was collected at an aeration pond, spring. The first sample was collected at the spring as a control. Since it was up gradient from site, it was not expected to have contaminants from the waste. The water was running at about 1.5m/s, it had a pH of ~6, temperature of ~18˚C, dissolved oxygen (DO) of ~7.75mg/L or 83%, and a conductivity of ~67µS/cm. The spring water was labeled AZ-311. The next water sample was taken at the smaller water body on the site. The water was stagnant and murky. It had a pH of ~7.1, temperature of ~22˚C, DO of ~12mg/L or 139%, and a conductivity of ~66.5µS/cm. This samples was labeled AZ-312. The final sample was taken at the larger pond. There is no field sheet for this sample. It was labeled AZ-313. After each water sample was collected, it was put through a 0.45µm filter into two 125mL bottle. One of the bottles had a red sticker for anion and the other had a yellow for cation.

In the lab, each sample was divided into an A and B to provide two data sets. Each of the samples was labeled with an A or B at the end – ex. T1-S1-A – and put into

50mL centrifuge tubes. The water samples did not need any initial preparation. They were just divided into separate A and B data sets and anion, cation tubes. Soil samples were mixed with deionized water (DI) to collect leachate. 40mL of DI were measured out into the tube, followed by 4g of soil sample. The samples were manually shaken for approximately 5 minutes, and left to settle for a little over 4hrs. The samples were then decanted into smaller containers and filtered into new tubes with the same label plus *filtered* using a 0.45µm filter. The filters were changed and measuring instruments cleaned between each sample to avoid cross contamination. All of the sediment settling was done on May 12th, 2012 at approximately 9:30am. Only samples T1-S1 to T1-S9 and T3-S5-B were filtered on May 12th 4hrs after shaking. The rest of the samples were filtered on May 13th at 9:30am. Each tube had ~20mL of filtered leachate.

After prep, the leachate and water samples were ready to be tested in the lab. For the anion testing, each sample was run through the HPIC and tested for chloride, sulphate, nitrate, and phosphate. A seven-anion standard was used as an indicator for each of the anions. 1g of standard was mixed with 10g of DI to create a standard solution. 5mL of filtered sample was placed into the HPIC tubes and labeled accordingly. They were then run through the machine in order preceded by two blanks (DI), the standard, and another blank, then were followed by a blank, standard and blank.

The cations were tested using the AAS. Three cations were tested (Na, Ca, Mg). Ca was run first using standards of 50ppm, 15.85ppm and 5ppm. The AAS was calibrated with the highest standard and then each standard was run from lowest to highest followed by each sample individually. The next was Mg, which used standards of 6.67ppm, 17.91ppm, 35.74ppm. Finally, Na was run using 22.00ppm, 11.285ppm and

6.85ppm standards. The Na concentrations were very high, so they were all diluted by a factor of 10. T1-S2-A was diluted by 20 and T1-S5-A was diluted by 30. When calculating final concentrations, the values were multiplied by the amount they were diluted to get the true value, so by 10, 20 or 30 times respectively.

There were some peculiarities during the lab work. T1-S2-A and T1-S5-A both had a yellow color after they were filtered. This could have meant that there were suspended solids that were too small for the 0.45µm filters. The cation testing had to be run multiple times to find the proper standards that would cover the high concentrations. There was also a great time constraint on preparation, experimentation and analysis.

Results

Once the raw data was acquired, it was organized into a more logical format. The values for the standards and retests were removed, and the usable values were compiled and organized by their cation ion or anion type, Ca, Mg, Chloride…ect. The data was then further broken down into the A and B Data Sets. Once the data was separated by data set and ion, it was easier to create various graphs and statistics. A statistical table – see *Stats Table* in appendix – was created and sorted by the ion and transect tested. For example, T1-Ca, T2-Ca or AZ-Chloride. For each row, the average of Data Set A and B individually (avg. A; avg. B), standard deviation of A and B individually (Std dev-A; Std dev-B), average of A and B combined (avg. A,B), and the standard deviation of A and B combined (Std dev-A,B) were found. Outliers were excluded from the statistical analysis. Four main types of scatter-plot graphs were created; a data set comparison of each ion on each transect, and a data set comparison of each ion over all transects; a

transect comparison for each ion of each data set; an ion comparison for each transect. For all graphs, the Y-axis is the concentration and the X-axis is the sample. With the exception of the overall data set comparisons, the x-value correlates with the sample placement on the transect. Each transect begins at the x-value one, and the following sample increase the x-value by one. For example, both T1-S1 and T3-S4 would have a x-value of one because they start their transect.

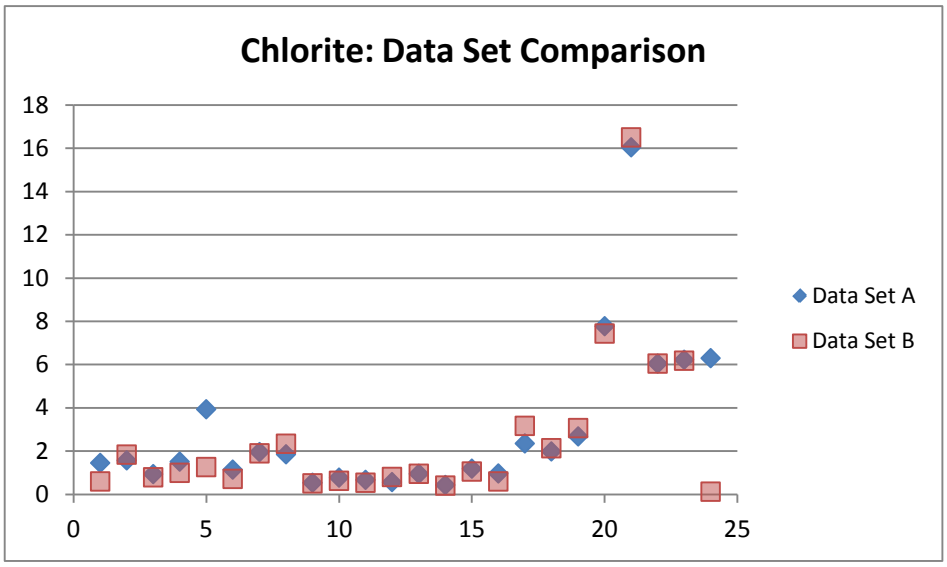

Figure 2. - *Compares Data Sets of all Chloride Samples*

Figure 2. above is an example of an overall data set comparison. It depicts all of the transects for each anion or cation, and places one data set on top of the other. This gauges the precision by comparing the two data sets for each sample. Generally, these graphs matched up well with some variation.

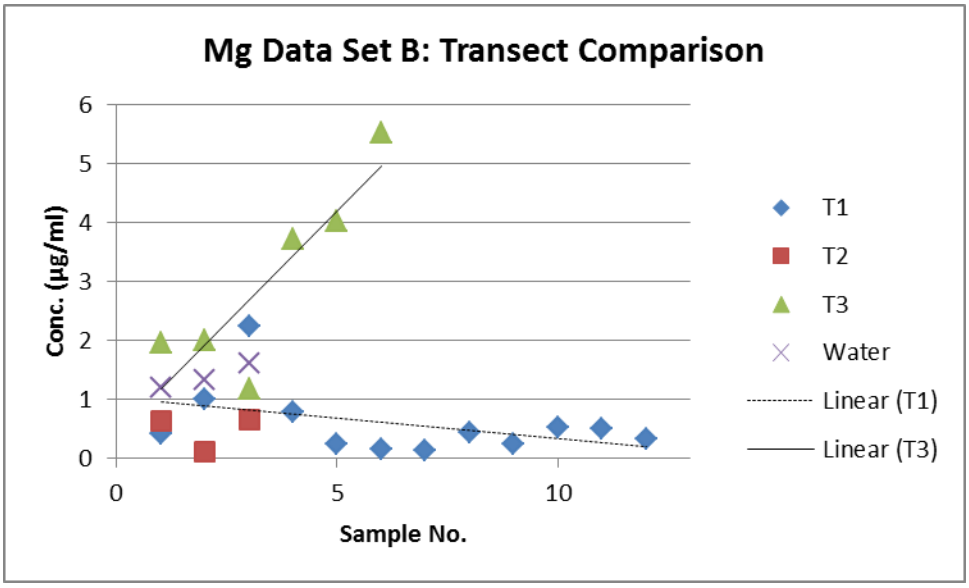

Figure 3. - *Compares Concentration of Mg on All Transects*

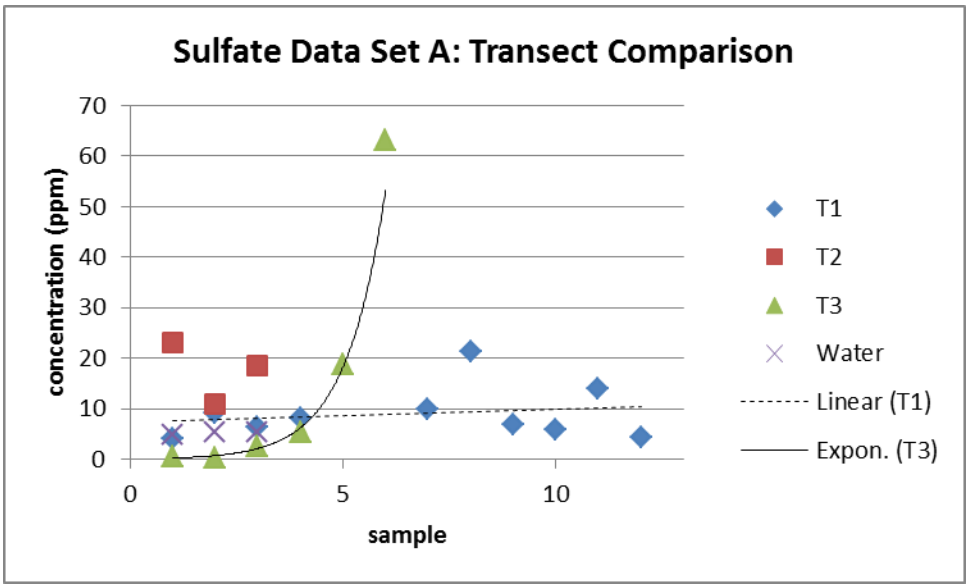

Figure 4. - *Compares Concentration of Sulfate for All Transects*

Figure 3. and Figure 4. both are transect comparisons. Figure 3. shows the trends of the Mg Data Set B transects. Transect 3 shows a strong, positively correlating, linear trend. This is consistent with the other cations. Transect 1 on this figure has a slightly negative trend. This is consistent with Na but not Ca. As seen in the appendix, both Mg and Na have weak negative correlations, while Ca has a slightly stronger and positive

correlation. Figure 4. compares the Sulfate Data Set A transects. Transect 1 is a very weakly correlating, positive trend. Data Set B shows a slightly stronger positive trend but still with a low slope. Chlorite was the only other anion graphed this way. It also had a weak trend but in the negative direction. Transect 3 has a very strong trend. As the samples continue along the transect, the concentration follows an exponential curve. Both data sets and anions follow this general trend.

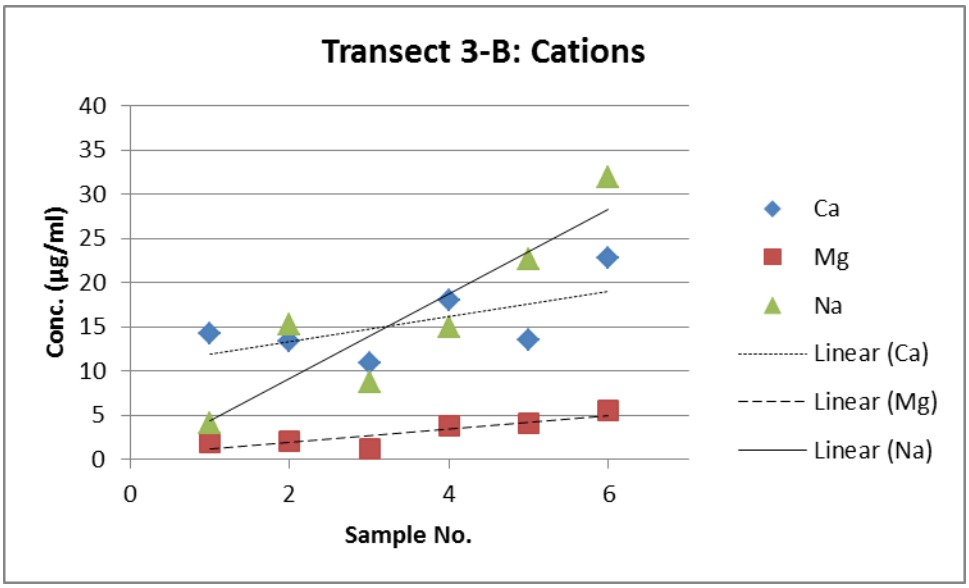

Figure 5. - *Detailed Depiction of Cations in Transect 3*

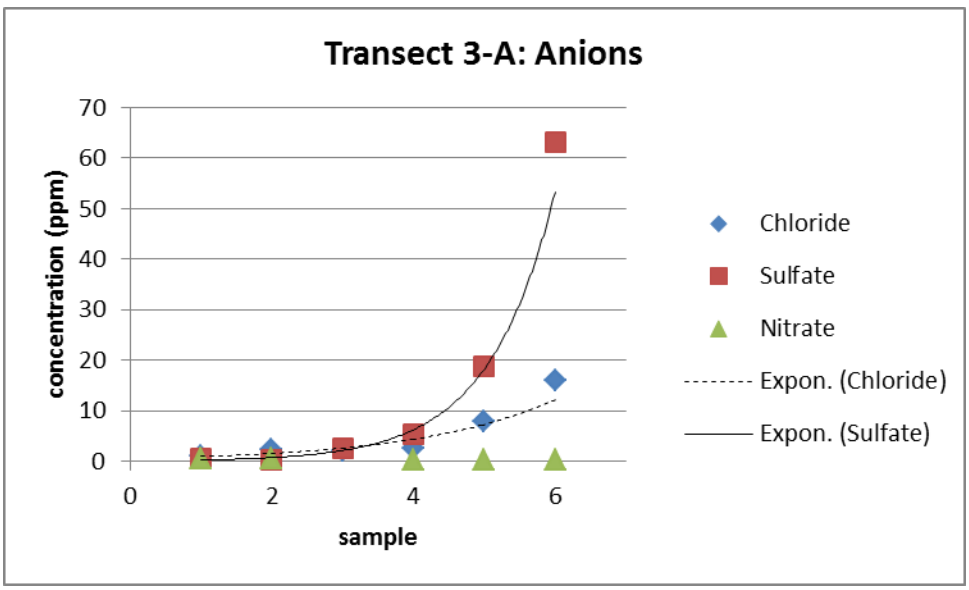

Figure 6. - *Detailed Depiction of Anions in Transect 3*

Figure 5 and Figure 6. graph individual transects. These graphs display the concentration of all anions or cations found from the beginning to the end of the transect. They are used to view each transect in detail as opposed to each ion. Figure 5 represents the cations of Transect 3, Data Set B. As observed before, Transect 3 cations had a strong positive trend. This breaks the graph down to show the trends of the individual cations. It shows Na with a strong trend, Ca with a moderate trend and Mg with a slightly weaker trend and lower concentrations. Data Set A shows the same. As seen in the appendix, Transect 1 has a positive correlation for Ca and a fairly negligible trend or correlation for Na and Mg. Figure 6. plots the anions for Transect 3, Data Set A. Figure 4. demonstrated that Transect 3 had an exponential trend. Figure 6. illustrates that sulfate has a strong curve and chloride has a gentler curve. Nitrate shows an insignificant trend, and was overall disregarded based on results and incomplete raw data. Data Set B generally follows the same trends.

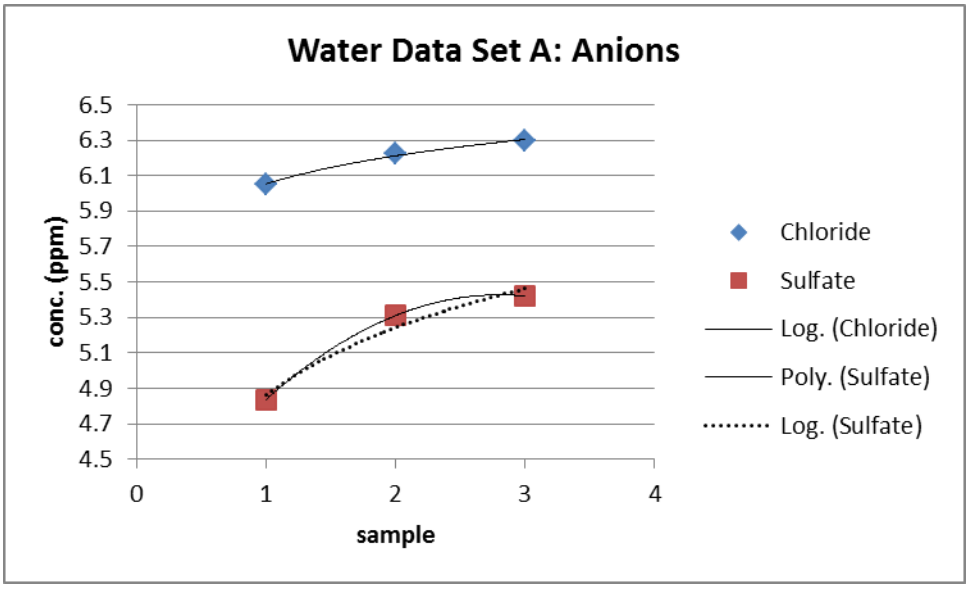

Figure 7. - *Shows Logarithmic Trends of Anions in Water Samples*

Figure 7. is another transect graph. It depicts the anions in the water samples. Only Data Set A was graphed because Data Set B had inconsistent results most likely due to mistakes during lab experimentation. There is limited data but the graph shows interesting trends. Chlorite and sulfate show logarithmic trends. These are different from the cations that were variable based on site, with some slight patterns.

Discussion

Two data sets were tested in order to verify the results for each of the samples. The Data Set Comparison graphs, such as Figure 2. and the others in the appendix, strengthen the results. Most of the samples from the data sets were very similar or almost exact. However, there were some exceptions. T1-S2-A and T1-S5-A were both extremely high in concentration. This could be explained by the yellow color they displayed. The color was most likely due to fine sediments getting through the filter. Other inconsistencies, such as AZ-313-B indicating significantly lower concentrations of anions, could be due to human error in the lab. Over all, the graphs showed consistency.

The concentrations of ions seemed to be predominantly controlled by the location of their transect. Transect 2 did not have enough data points to produce trends, so it was not considered during the interpretation of the results. Transect 1 ran from the edge of the larger water body towards the waste site. It was located the furthest away from the central site and often had some grass covering the sediment. It most likely contained the oldest waste material. Transect 3 was located on the exposed sediment and proceeded further towards the site center at a slight angle. It probably was relatively new waste material.

Transect 1 resulted in an upward trend for Ca away from the pond, and a flat, slightly negative trend for Na and Mg. This could be due to the absorption of these ions by plants. As Transect 1 progresses, it goes from a water source to vegetation. Plants may preferentially absorb the Mg and Na, so their concentration does not increase as it gets closer to the waste and vegetation, like Ca. It could also be due to runoff taking away Na, and Mg to the water, while Ca has been adsorbed by the soil. For the anions, sulfate had a small upward sloping trend, while chloride had a slight negative slope. This may be due to the solubility of the anions. Both dissolve easily in water, but there are more sulfates than chlorides that do not easily dissolve in water. As a result, runoff takes more chlorides toward the water than sulfates and gives the opposing weak trends.

Transect 3 is located on the exposed solid waste sediment. The further down the transect, the closer to the center of the waste site the samples were. The cation results returned a strong increasing trend as the samples were taken closer to the center of the site. The most positive trend was the Na. Ca had the next strongest and Mg the weakest. The most logical thought is that the closer to where the most waste is dumped, the higher the concentrations will be. One possible explanation is that there is an age trend. The sediment closer to the center may be newer than the more distant. Based on wind or other factors there could be bias in the dispersion of waste material around the site. The reason for the differences in the cation trends is not as clear. Like Transect 1 solubility and adsorption are plausible reasons. There is no vegetation to absorb ions or facilitate infiltration. As a result, soil adsorption and runoff could increase at this location. Ca and Mg might have been adsorbed into the soil quickly, so they were less prone to washing away with the runoff. Na was easily taken by runoff, but closer to the center new

material takes its place. This explains Na's steep gradient. Ca and Mg increased at more similar rates. The reason Mg had less slope because there is less of it around. This accounts for the lower overall concentration and less increase compared to Ca closer to the site center. Initial concentration may also be the reason for sodium's overall higher concentration. The anions displayed an exponential trend in Transect 3. Sulfate had a rapidly increasing trend, and chloride's curve was more gradual. Nitrate had very low concentrations and did not show any clear trends. The same theory regarding solubility can be used to explain why the curves were exponential. Overall, more sulfates seem to be in the sediment than chloride, so it has a higher value in the newer material closer to the center. Both of these anions are very soluble, so they rapidly decrease as distance away from the waste source increases. Based on the anion graphs for Transect 3, it seems like a similar ratio of sulfate to chloride in the sediment follows throughout the curve. So the reason chloride has such a gentler curve is based on its original concentration.

The anion water samples created logarithmic trends. This is very different from the cations that showed a slight increasing trend for Ca and Mg and more up and down result for Na. Since there were only three sites, the data is very limited and difficult to infer trends with. Overall, it seemed like concentrations were increasing from AZ-311 to AZ-313. This could be explained by their location and contact with the waste site. AZ-311 was from the spring source. This was used as a control. AZ-312 is from the smaller water body that looks closer to the waste site, and AZ-313 is the larger water body. It makes sense the spring water would have the lowest level of contaminants. If the smaller water body is closer to the site then why does it have fewer pollutants? Based on the site map, the larger water body looked more polluted to the naked eye. There was also a

sediment flow pattern from the waste site that looked like it lead into the larger water body. The larger body could have been more hydrologically connected to the waste site than the closer small body. The smaller body could also have been supplied by the spring, which feeds it fresher water. Figure 7. can help strengthen the solubility argument. In the spring, chloride is much more prevalent which could be a factor of its slightly higher solubility. Also chloride increases at a slightly faster rate, which could be due to more flowing in from runoff.

Some of these results were somewhat expected, while other were not. It was hypothesized that as samples were taken closer to the waste site or further removed from the spring, they would increase in contaminants. This was true, but some of the individual ion behaviors were not expected. The exponential curve was surprising. Linear curves were expected because extreme changes in concentration were not thought to occur over small transects. The possible connection with solubility and adsorption in soil was similar to what was predicted based on prior research of these concepts.

The data came out fairly well, but there must be more. There is simply not enough data to confidently draw conclusions from these results. Everything is speculation. The lab methods were good for the time constraint of the experiment, but it would be better to have more extensive work done. This would mean more repetitions, variation in sediment volume, and changes in chemical characteristics such as pH.

Further research must be done on the subject. The most important is gathering more data to feed into the results and strengthen the trends. Other experiments could help as well. A more extensive test could look into organics and heavy metals. This could help draw conclusions about how the tested ions are linked to these often more dangerous

toxins. In order to get a more extensive spatial trend, new transects that cover more distances should be measured. Ideally, transects that run from the water bodies across the waste site and to the Tarawera River would provide a large spatial database and much more insight.

Conclusion

It is paramount to gain as much information as possible about contamination sites like Lake Rotoitipaku. Not only is the area extremely susceptible to large environmental risks due to natural geologic factors, it is a site that is of major cultural significance to a local people. Society has come a long way in making sure natural sites like these are preserved in the future, but the lingering effects of past decisions are still a prevalent danger. Research into trends of contaminants at these locations will help scientists contain the damaged areas, and hopefully restore them and the surrounding area. It will also provide a guide for other environmental scientists or waste site developers to follow and learn from past mistakes. This paper focus on the trends of the concentrations of specific anions and cations in order to find spatial and temporal trends that would help assess the condition of the waste site and the surrounding area. Although there is an unsatisfactory amount of data points, the solid waste leachate and water sample tests suggests there are significant trends of contamination based on location and time. Transects closer to the center of the site had higher contamination levels. Data, such as Transect 1, seems to represent an older area of the contamination site that has been more greatly affected by disturbing conditions such as vegetation, runoff, adsorption and infiltration. Upon further research these trends can be strengthened and augmented with more data points and tests for other toxins, and provide vital insight to the health of the

system.

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Appendix:

Raw Data:

Cation – Ca Data Table (set A and B)

data set A			
Ca			
Sample Label	Conc. (µg/ml)	%RSD	Mean Abs.
Standard 1	5	0.55	0.1301
Standard 2	15	0.97	0.3472
Standard 3	50	1.33	0.7574
T1S1A	11.916	0.06	0.2665
T1S2A	4.429	1.03	0.109
T1S3A	14.885	3.74	0.3383
T1S4A	9.325	1.17	0.2154
T1S5A	29.461	6.7	0.5564
T1S6A	15.646	2.14	0.3347
T1S7A	12.802	1.45	0.2997
T1S8A	24.286	2.63	0.488
T1S9A	15.076	1.64	0.3418
T1S10A	22.408	0.78	0.4609
T1S11A	16.275	5.14	0.3629
T1S12A	14.178	6.62	0.3255
T2S1A	30.789	1.86	0.5727
T2S2A	17.235	0.65	0.3793
T2S3A	27.616	3.25	0.533
T3S4A	11.958	2.54	0.2834
T3S5A	10.549	1.63	0.2552
T3S6A	14.515	2.58	0.3316
T3S7A	18.141	4.89	0.3944
T3S8A	10.451	4.65	0.2532
T3S9A	24.639	2.57	0.4929
AZ311A	0.802	2.28	0.0227
AZ312A	0.857	2.86	0.0242
AZ313A	2.57	6.04	0.0705

data set B			
Ca			
Sample Label	Conc. (µg/ml)	%RSD	Mean Abs.
Standard 1	5	0.55	0.1301
Standard 2	15	0.97	0.3472
Standard 3	50	1.33	0.7574
T1S1B	9.352	3.16	0.2159
T1S2B	5.481	2.94	0.133
T1S3B	12.971	0.88	0.3029
T1S4B	15.412	3.8	0.3306
T1S5B	15.785	1.05	0.3543
T1S6B	14.248	3.61	0.3268
T1S7B	12.631	0.32	0.2964
T1S8B	28.437	1.41	0.5436
T1S9B	7.787	6.82	0.1965
T1S10B	22.068	1.4	0.4559
T1S11B	17.371	0.65	0.3816
T1S12B	13.84	3.78	0.3192
T2S1B	29.805	3.12	0.5607
T2S2B	18.065	5.74	0.3932
T2S3B	22.263	4.67	0.4588
T3S4B	14.238	1.39	0.3266
T3S5B	13.369	3.24	0.3105
T3S6B	10.867	3.9	0.2617
T3S7B	17.964	0.7	0.3915
T3S8B	13.464	4.36	0.3122
T3S9B	22.701	2.5	0.4652
AZ311B	0.901	9.07	0.0254
AZ312B	0.968	12.56	0.0273
AZ313B	2.563	1.14	0.0704

Cation – Mg Data Table (set A and B)

data set a			
Mg			
Sample Label	Conc. (µg/ml)	%RSD	Mean Abs.
Standard 1	6.67	0.04	0.337
Standard 2	17.91	0.56	0.7936
Standard 3	35.74	0.16	1.3496
T1S1A	0.289	11.33	0.0157
T1S2A	1.475	0.74	0.0791
T1S3A	2.66	0.37	0.1405
T1S4A	0.773	1.14	0.0418
T1S5A	0.25	1.45	0.0136
T1S6A	0.121	16.5	0.0066
T1S7A	0.182	8.77	0.0099
T1S8A	0.318	7.34	0.0173
T1S9A	0.238	5.3	0.013
T1S10A	0.618	1.76	0.0335
T1S11A	0.551	4.93	0.0298
T1S12A	0.352	7.67	0.0192
T2S1A	0.49	19.77	0.0266
T2S2A	0.141	8.04	0.0077
T2S3A	0.722	3.44	0.039
T3S4A	1.883	0.66	0.1004
T3S5A	3.13	0.52	0.1644
T3S6A	2.008	0.67	0.1069
T3S7A	4.07	1.03	0.2114
T3S8A	2.955	0.25	0.1555
T3S9A	7.18	0.36	0.3595
AZ311A	1.188	0.74	0.0639
AZ312A	1.336	1.61	0.0717
AZ313A	1.611	0.41	0.0862

data set b			
Mg			
Sample Label	Conc. (µg/ml)	%RSD	Mean Abs.
Standard 1	6.67	0.04	0.337
Standard 2	17.91	0.56	0.7936
Standard 3	35.74	0.16	1.3496
T1S1B	0.417	7.13	0.0226
T1S2B	1	9.27	0.0208
T1S3B	2.233	1.2	0.1186
T1S4B	0.788	3.16	0.0426
T1S5B	0.248	8.04	0.0135
T1S6B	0.151	4.02	0.0082
T1S7B	0.132	12.19	0.0072
T1S8B	0.435	5.55	0.0236
T1S9B	0.245	6.04	0.0134
T1S10B	0.521	3.08	0.0283
T1S11B	0.497	2.82	0.027
T1S12B	0.338	6.03	0.0184
T2S1B	0.633	4.87	0.0343
T2S2B	0.119	6.41	0.0065
T2S3B	0.656	1.23	0.0355
T3S4B	1.968	0.54	0.1048
T3S5B	1.998	1.21	0.1064
T3S6B	1.187	1.57	0.0638
T3S7B	3.725	0.48	0.1942
T3S8B	4.025	1.12	0.2092
T3S9B	5.528	0.82	0.2822
AZ311B	1.201	2.88	0.0646
AZ312B	1.333	0.39	0.0716
AZ313B	1.606	0.92	0.086

Cation – Na Data Table (set A and B)

data set a				
Na		new		
Sample Label	Conc. (µg/ml)	Conc. (µg/ml)	%RSD	Mean Abs.
Standard 1	6.85		1.44	0.3151
Standard 2	11.285		0.91	0.5798
Standard 3	22		0.69	1.1242
T1S1A	0.243	2.43	11.91	0.0112
T1S2A	18.157	363.14	0.96	0.9226
T1S2a	18.246	364.92	0.17	0.9276
T1S3A	0.282	2.82	15.76	0.013
T1S4A	2.047	20.47	0.79	0.0951
T1S5A	16.774	503.22	1.21	0.8455
T1S6A	0.191	1.91	18.37	0.0088
T1S7A	0.92	9.2	15.35	0.0425
T1S8A	0.155	1.55	7.78	0.0071
T1S9A	0.076	0.76	HIGH	0.0035
T1S10A	0.102	1.02	HIGH	0.0047
T1S11A	0.1	1	14.95	0.0046
T1S12A	0.072	0.72	HIGH	0.0033
T2S1A	0.128	1.28	HIGH	0.0059
T2S2A	0.133	1.33	5.73	0.0061
T2S3A	0.102	1.02	HIGH	0.0047
T3S4A	0.444	4.44	4.01	0.0204
T3S5A	1.362	13.62	2.42	0.063
T3S6A	0.971	9.71	6.32	0.0448
T3S7A	1.421	14.21	1.01	0.0658
T3S8A	2.33	23.3	0.29	0.1083
T3S9A	3.635	36.35	1.02	0.1702
AZ311A	0.927	9.27	4.71	0.0428
AZ312A	0.847	8.47	1.23	0.0391
AZ313A	0.865	8.65	2.4	0.0399

data set b				
Na		new		
Sample Label	Conc. (µg/ml)	Conc. (µg/ml)	%RSD	
Standard 1	6.85		1.44	0.3151
Standard 2	11.285		0.91	0.5798
Standard 3	22		0.69	1.1242
T1S1B	2.395	23.95	1.15	0.1114
T1S3B	0.177	1.77	HIGH	0.0081
T1S4B	0.135	1.35	13.83	0.0062
T1S5B	0.134	1.34	13.56	0.0061
T1S6B	0.087	0.87	HIGH	0.004
T1S7B	0.146	1.46	HIGH	0.0067
T1S8B	0.28	2.8	HIGH	0.0129
T1S9B	0.99	9.9	2.14	0.0457
T1S10B	0.121	1.21	HIGH	0.0055
T1S11B	0.096	0.96	HIGH	0.0044
T1S12B	0.136	1.36	18.2	0.0062
T2S1B	0.078	0.78	HIGH	0.0036
T2S2B	0	0	HIGH	-0.0007
T2S3B	0.144	1.44	18.31	0.0066
T3S4B	0.409	4.09	18.81	0.0188
T3S5B	1.527	15.27	1.71	0.0707
T3S6B	0.865	8.65	4.04	0.0399
T3S7B	1.5	15	6.5	0.0694
T3S8B	2.262	22.62	1.69	0.1052
T3S9B	3.191	31.91	0.69	0.1491
AZ311B	2.294	22.94	1.45	0.1067
AZ312B	0.868	8.68	3.74	0.04
AZ313B	0.857	8.57	8.49	0.0395

chloride	
sample	conc. (ppm)
T1S1A	1.4521
T1S1B	0.5935
T1S2A	1.5708
T1S2B	1.8325
T1S3A	0.9295
T1S3B	0.7882
T1S4A	1.5091
T1S4B	0.9974
T1S5A	3.9306
T1S5B	1.2563
T1S6A	1.1435
T1S6B	0.7184
T1S7A	1.9534
T1S7B	1.8874
T1S8A	1.8515
T1S8B	2.3356
T1S9A	0.5317
T1S9B	0.512
T1S10A	0.7689
T1S10B	0.624
T1S11A	0.6726
T1S11B	0.5339
T1S12A	0.5709
T1S12B	0.8056
T2S1A	0.9526
T2S1B	0.9466
T2S2A	0.4362
T2S2B	0.4063
T2S3A	1.1907
T2S3B	1.0479
T3S4A	0.961
T3S4B	0.589
T3S5A	2.3541
T3S5B	3.1582
T3S6A	1.9808
T3S6B	2.1326
T3S7A	2.6781
T3S7B	3.0552
T3S8A	7.7695
T3S8B	7.4353
T3S9A	16.0469
T3S9B	16.505
AZ311A	6.0491
AZ311B	6.0417
AZ312A	6.2226
AZ312B	6.174
AZ313A	6.2967
AZ313B	0.1285

Sulfate	
sample	conc. (ppm)
T1S1A	4.0775
T1S1B	4.5952
T1S2A	9.1745
T1S2B	4.4566
T1S3A	6.4958
T1S3B	6.5463
T1S4A	8.128
T1S4B	8.1602
T1S5A	n/a
T1S5B	n/a
T1S6A	n/a
T1S6B	7.7228
T1S7A	9.9551
T1S7B	9.9202
T1S8A	21.4312
T1S8B	27.8437
T1S9A	6.9365
T1S9B	6.9182
T1S10A	5.7825
T1S10B	5.752
T1S11A	14.0756
T1S11B	13.2314
T1S12A	4.2162
T1S12B	4.235
T2S1A	23.1251
T2S1B	30.69
T2S2A	10.9605
T2S2B	10.6438
T2S3A	18.5129
T2S3B	16.8695
T3S4A	0.468
T3S4B	3.9576
T3S5A	0.3187
T3S5B	0.7272
T3S6A	2.4745
T3S6B	0.9793
T3S7A	5.3453
T3S7B	5.4913
T3S8A	18.8519
T3S8B	19.1993
T3S9A	63.1953
T3S9B	42.5695
AZ311A	4.8374
AZ311B	4.8173
AZ312A	5.3102
AZ312B	5.1685
AZ313A	5.4197
AZ313B	0.1141

Nitrate	
sample	conc. (ppm)
T1S1A	22.984
T1S1B	24.2113
T1S2A	n/a
T1S2B	11.907
T1S3A	78.1385
T1S3B	60.796
T1S4A	37.6012
T1S4B	37.9403
T1S5A	n/a
T1S5B	25.9135
T1S6A	15.0333
T1S6B	15.0934
T1S7A	10.9682
T1S7B	9.5109
T1S8A	1.7078
T1S8B	5.5153
T1S9A	0.414
T1S9B	0.3702
T1S10A	n/a
T1S10B	n/a
T1S11A	n/a
T1S11B	n/a
T1S12A	0.3787
T1S12B	0.3335
T2S1A	15.9321
T2S1B	19.1018
T2S2A	11.3709
T2S2B	10.3252
T2S3A	24.1179
T2S3B	21.7173
T3S4A	0.5101
T3S4B	7.6815
T3S5A	0.4761
T3S5B	0.1721
T3S6A	n/a
T3S6B	0.5091
T3S7A	0.1897
T3S7B	0.1646
T3S8A	0.3694
T3S8B	0.4086
T3S9A	0.3539
T3S9B	n/a
AZ311A	1.3306
AZ311B	1.151
AZ312A	0.0342
AZ312B	n/a
AZ313A	0.0313
AZ313B	0.0037

Phosphate	
sample	conc. (ppm
T1S1A	n/a
T1S1B	64.964
T1S2A	n/a
T1S2B	11.8811
T1S3A	n/a
T1S3B	n/a
T1S4A	53.9347
T1S4B	n/a
T1S5A	n/a
T1S5B	n/a
T1S6A	n/a
T1S6B	n/a
T1S7A	15.4417
T1S7B	n/a
T1S8A	n/a
T1S8B	n/a
T1S9A	n/a
T1S9B	32.2089
T1S10A	n/a
T1S10B	n/a
T1S11A	n/a
T1S11B	n/a
T1S12A	n/a
T1S12B	n/a
T2S1A	n/a
T2S1B	n/a
T2S2A	n/a
T2S2B	n/a
T2S3A	n/a
T2S3B	n/a
T3S4A	n/a
T3S4B	n/a
T3S5A	n/a
T3S5B	n/a
T3S6A	n/a
T3S6B	n/a
T3S7A	n/a
T3S7B	n/a
T3S8A	n/a
T3S8B	n/a
T3S9A	n/a
T3S9B	n/a
AZ311A	n/a
AZ311B	n/a
AZ312A	n/a
AZ312B	n/a
AZ313A	n/a
AZ313B	n/a

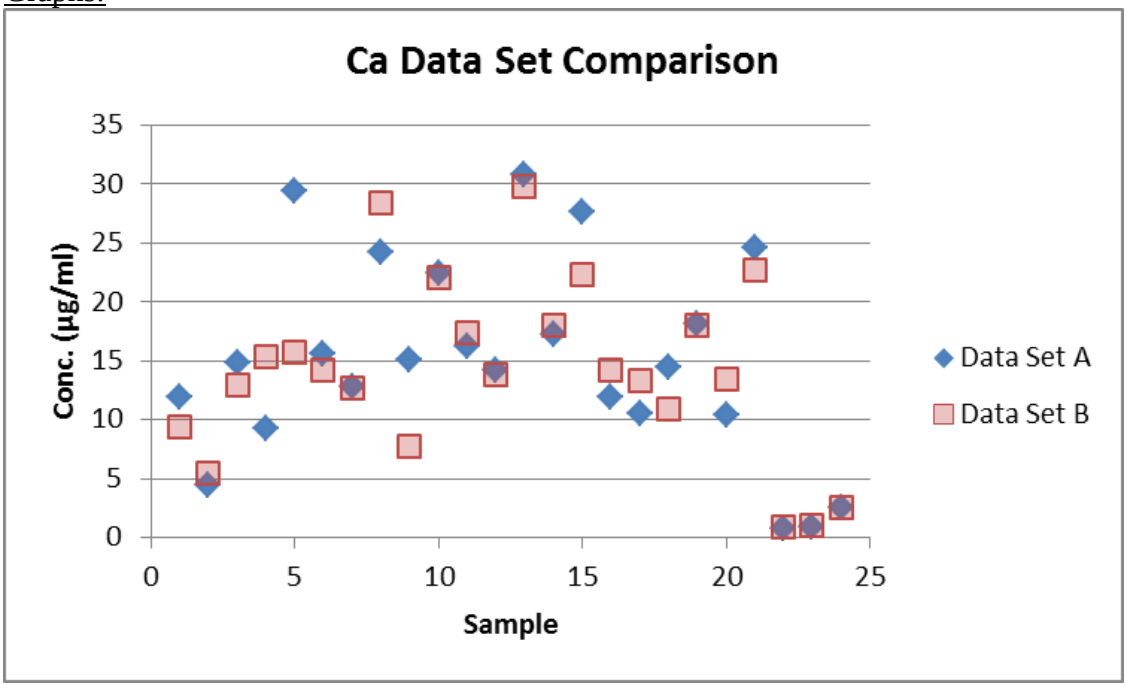
Anion Raw Data Table (above)

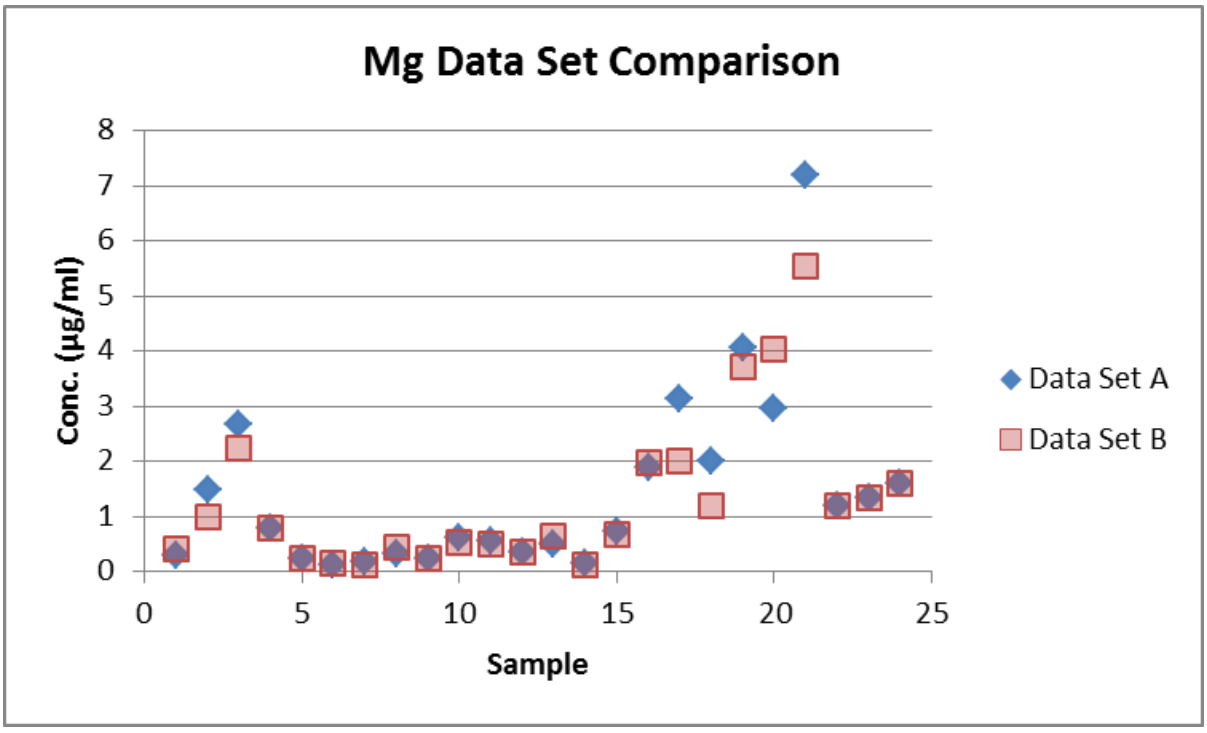
Statistics:

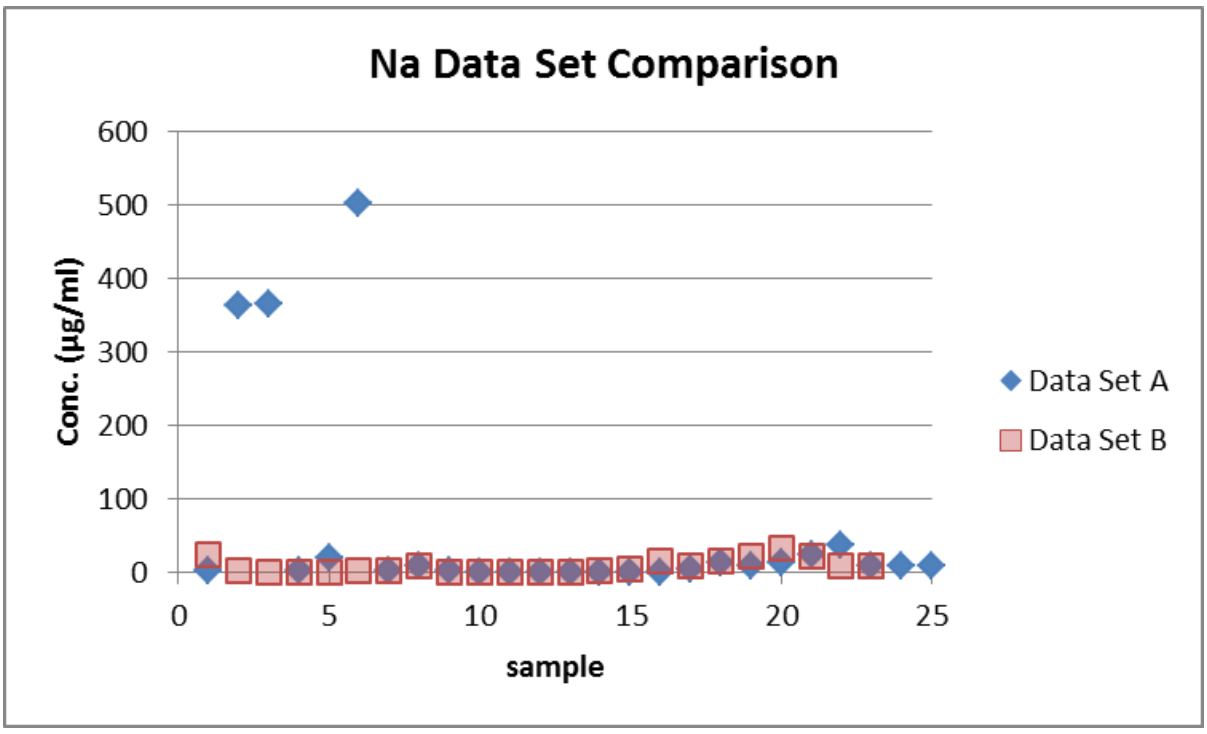
Stats Table

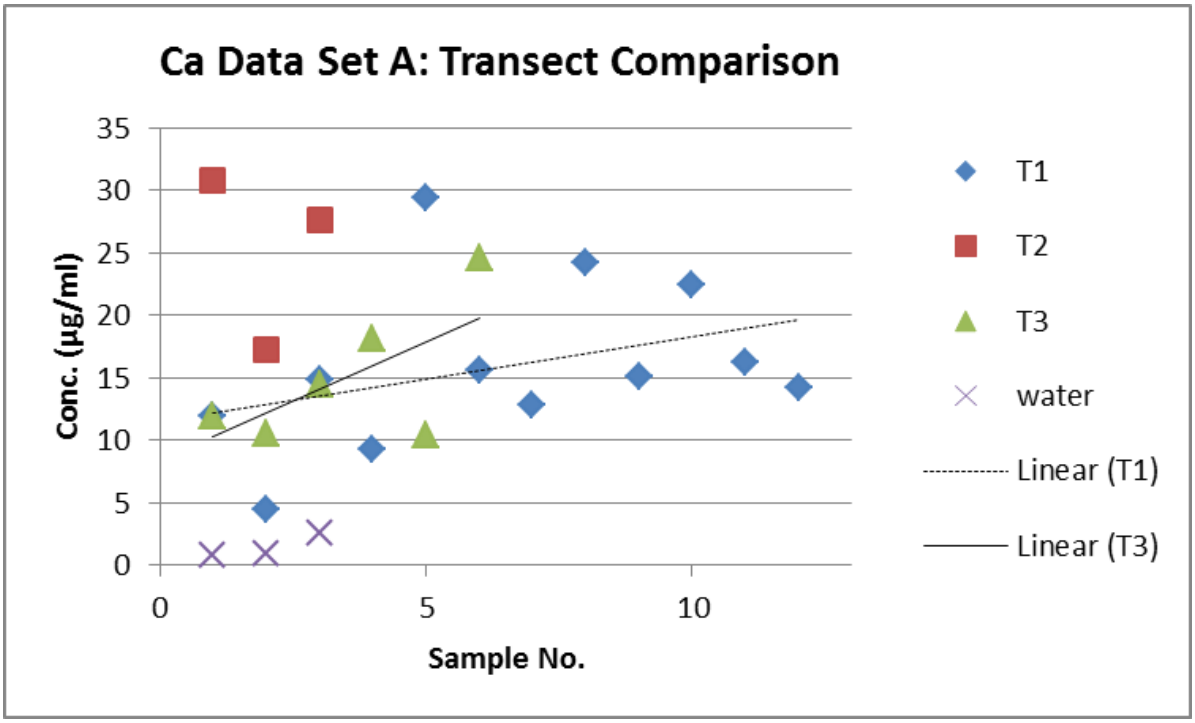
Sample	Avg.-A	Avg.-B	Std Dev-A	Std Dev-B	Avg. (A,B)	Std. dev (A,B)
T1-Ca	15.89058333	14.61525	6.753737	6.188843	15.25292	6.36847218
T2-Ca	25.21333333	23.37766667	7.089241	5.9488454	24.2955	5.938799534
T3-Ca	15.04216667	15.43383333	5.527374	4.2342229	15.238	4.698769201
AZ-Ca	1.409666667	1.477333333	1.005254	0.9408115	1.4435	0.871572544
T1-Mg	0.65225	0.58375	0.732652	0.5780552	2.852	0.643215158
T2-Mg	0.451	0.469333333	0.292457	0.3036154	0.460167	0.266807359
T3-Mg	3.537666667	3.071833333	1.956194	1.6304644	3.30475	1.734058252
AZ-Mg	1.378333333	1.38	0.214654	0.2065502	1.379167	0.188405325
T1-Na	4.188	4.27	6.247771	7.0197251	4.230952	6.496585184
T2-Na	1.21	0.74	0.166433	0.7208329	0.975	0.534031834
T3-Na	16.93833333	16.25666667	11.35073	9.9394239	16.5975	10.17818802
AZ-Na	8.796666667	13.39666667	0.419682	8.2649521	11.09667	5.808805959
T1-Chlor	1.40705	1.073733333	0.934838	0.6170885	1.240392	0.793137029
T2-Chlor	0.859833333	0.800266667	0.385709	0.3449242	0.83005	0.361520792
T3-Chlor	5.2984	5.479216667	5.779117	5.861249	5.388808	5.550268233
AZ-Chlor	6.189466667	4.114733333	0.127082	3.4528131	5.1521	2.463043367
T1-Sulf	9.02729	9.034690909	5.270348	6.7809573	9.031167	5.957362098
T2-Sulf	17.53283333	19.4011	6.141235	10.260082	18.46697	7.631562594
T3-Sulf	15.10895	12.15403333	24.55351	16.381435	13.63149	19.95979036
AZ-Sulf	5.1891	3.366633333	0.309463	2.8222447	4.277867	2.054446005
T1-Nitr	20.9032125	19.15914	26.46215	18.89533	19.93428	21.86662614
T2-Nitr	17.1403	17.0481	6.458817	5.9672647	17.0942	5.561688114
T3-Nitr	0.37984	1.78718	0.125667	3.2984174	1.08351	2.322185567
AZ-Nitr	0.465366667	0.57735	0.749315	0.8112636	0.51016	0.670101532

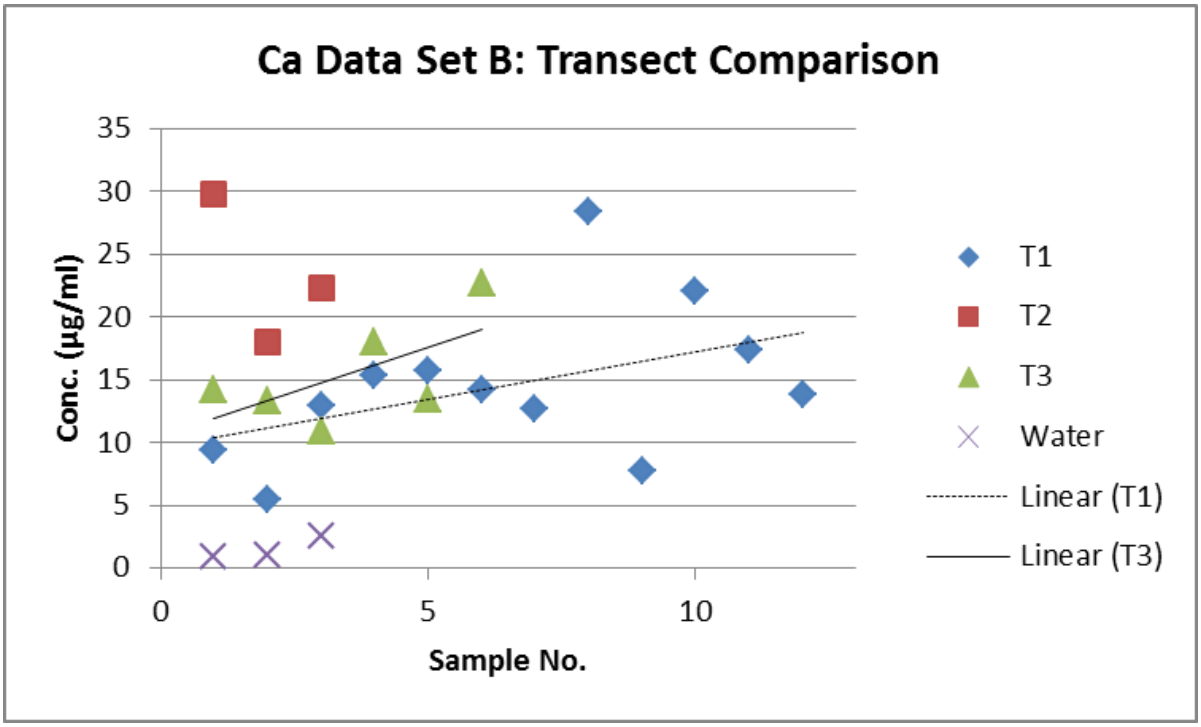
Graphs:

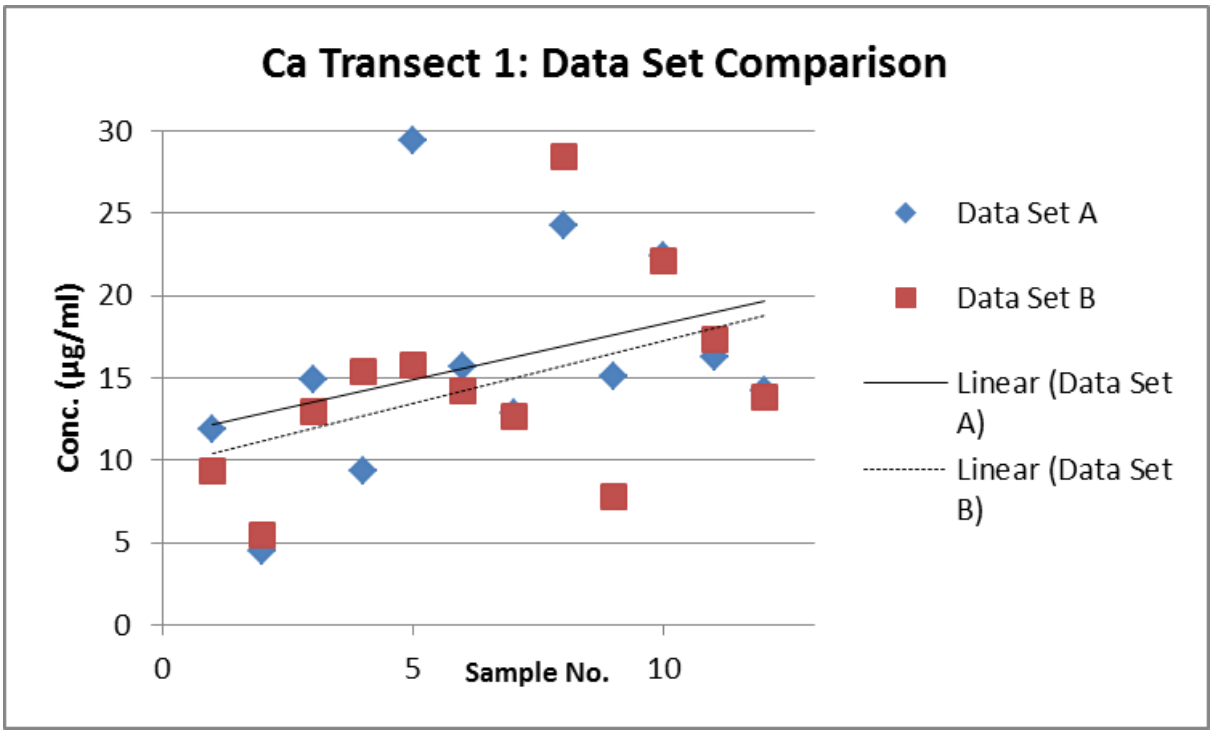


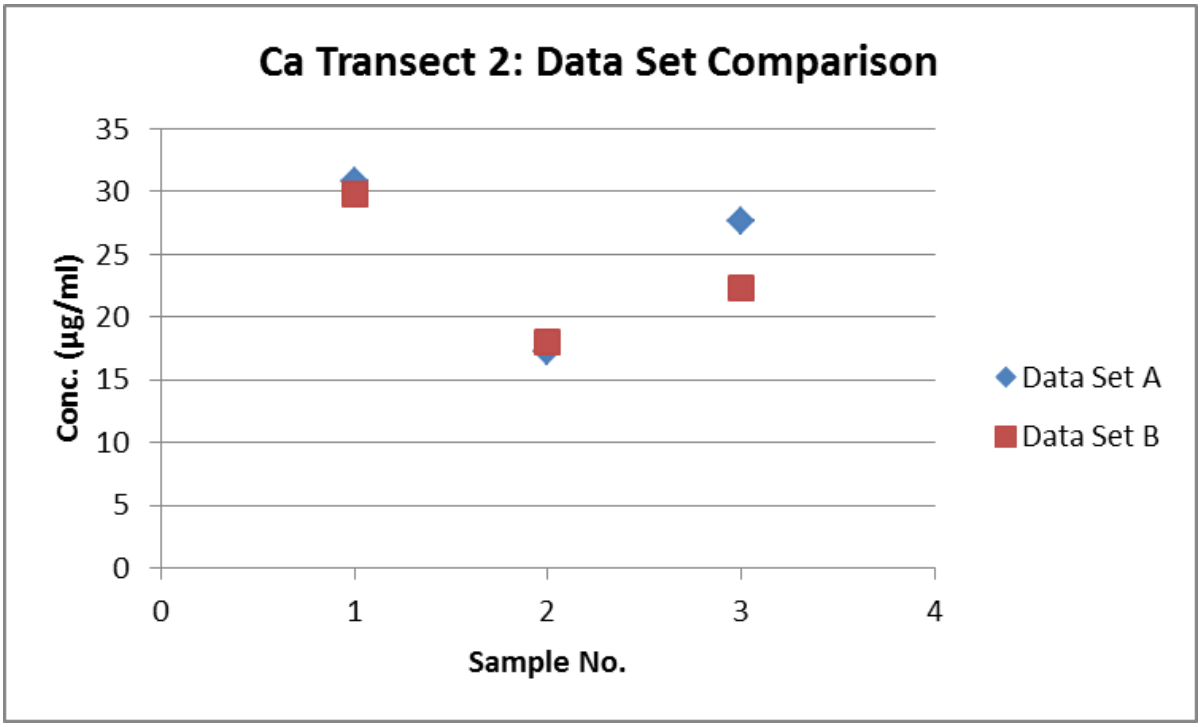

Mg Data Set Comparison
Conc. (µg/ml)
Sample
Data Set A
Data Set B

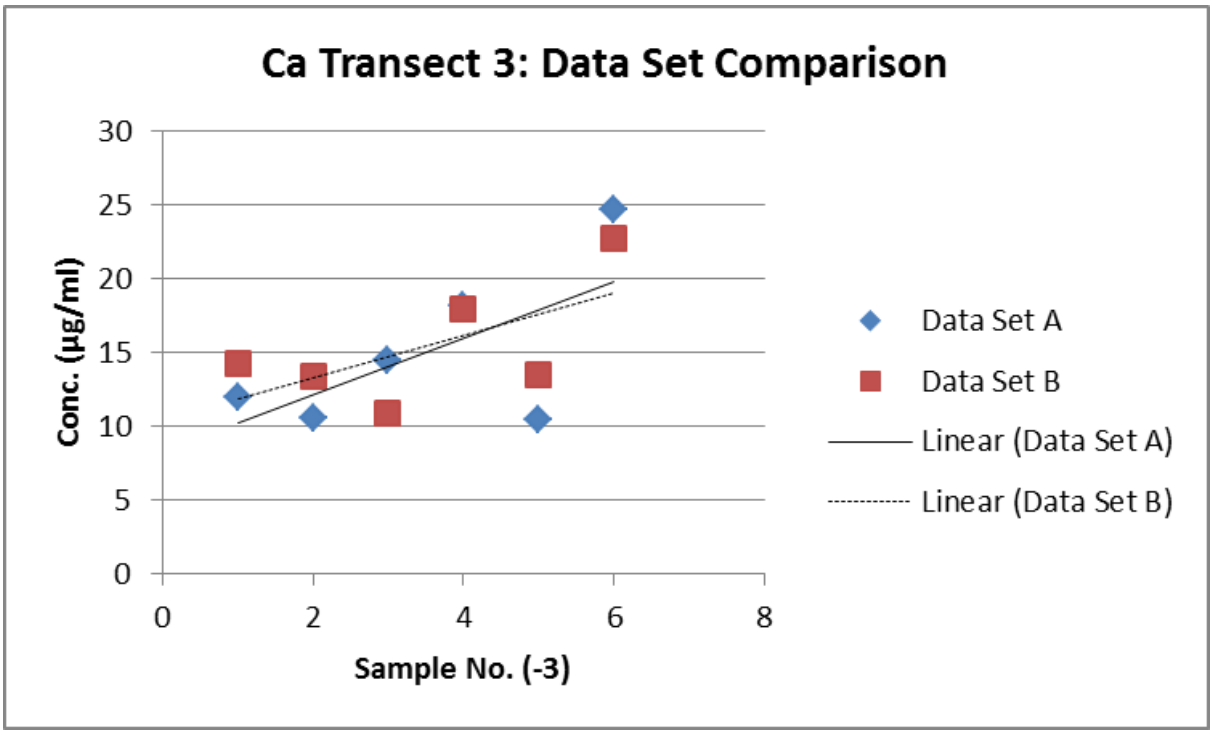

Na Data Set Comparison
Conc. (µg/ml)
sample
Data Set A
Data Set B

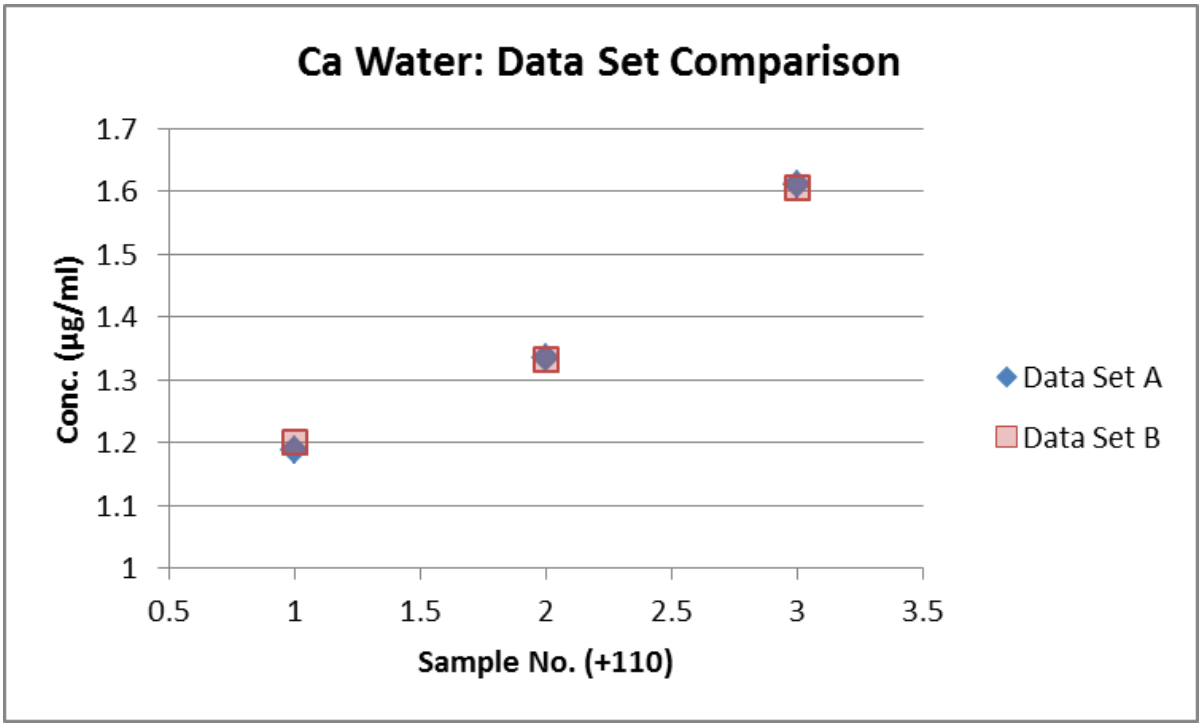

Ca Data Set A: Transect Comparison
Conc. (µg/ml)
35
30
25
20
15
10
5
0
0
5
10
Sample No.
T1
T2
T3
water
Linear (T1)
Linear (T3)

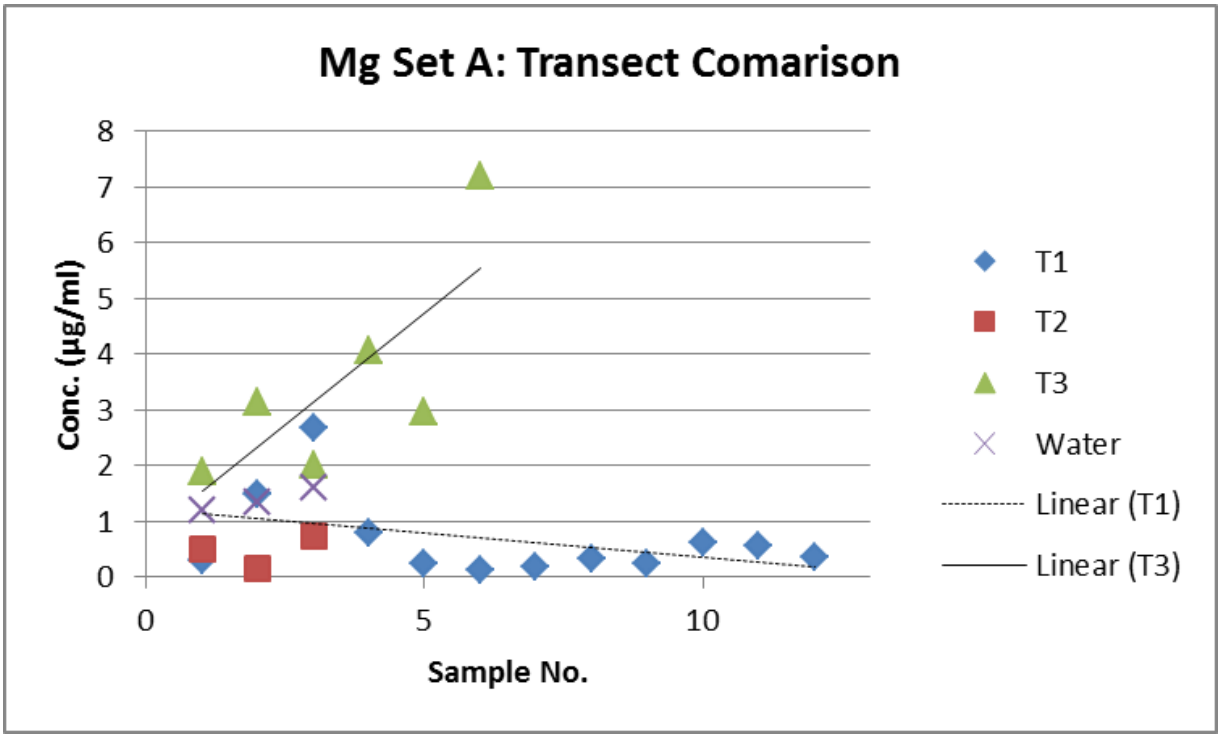

Ca Data Set B: Transect Comparison
Conc. (µg/ml)
35
30
25
20
15
10
5
0
0
5
10
Sample No.
T1
T2
T3
Water
Linear (T1)
Linear (T3)

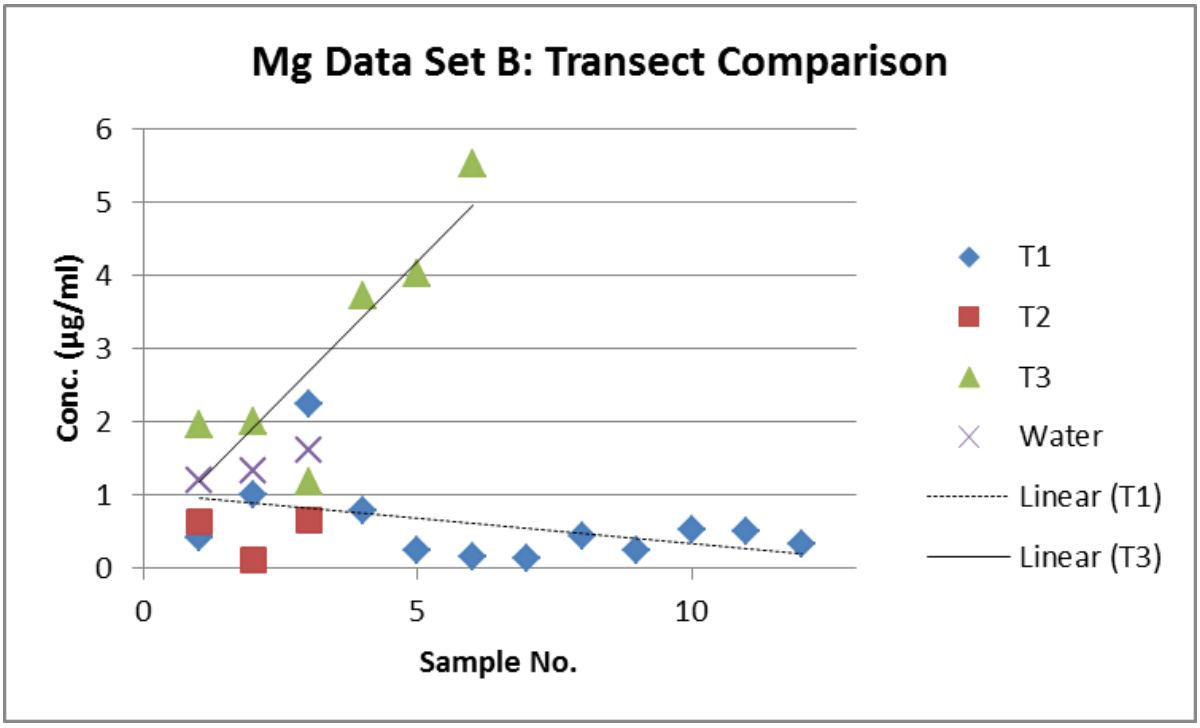

Ca Transect 1: Data Set Comparison
Conc. (µg/ml)
30
25
20
15
10
5
0
0
5
10
Sample No.
Data Set A
Data Set B
Linear (Data Set A)
Linear (Data Set B)

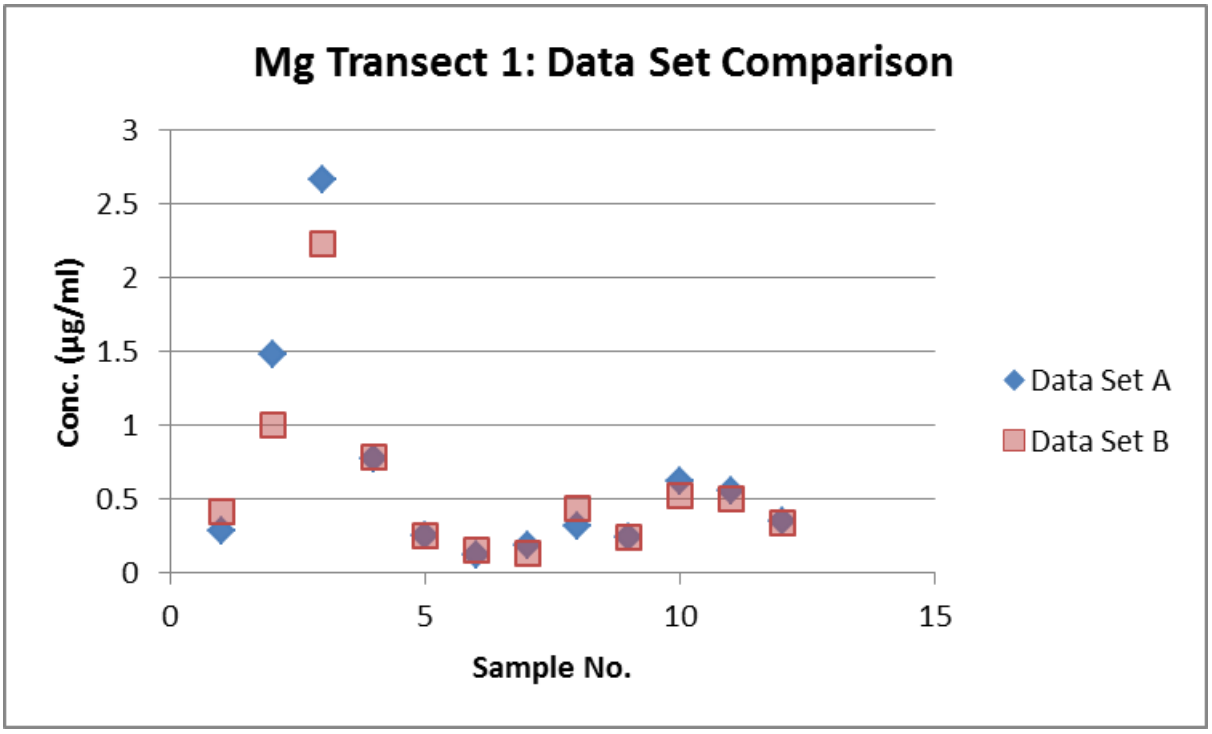

Ca Transect 2: Data Set Comparison
Conc. (µg/ml)
35
30
25
20
15
10
5
0
0
1
2
3
4
Sample No.
Data Set A
Data Set B

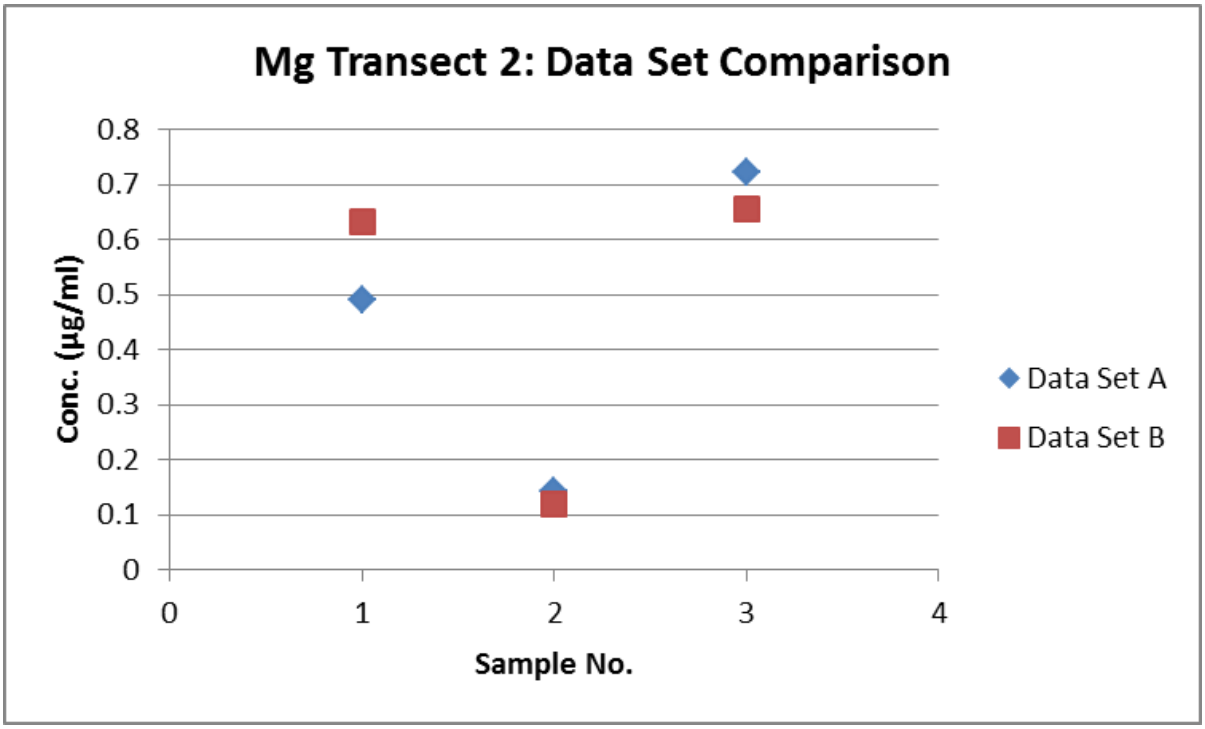

Ca Transect 3: Data Set Comparison
30
25
20
15
10
5
0
Conc. (µg/ml)
0
2
4
6
8
Sample No. (-3)
Data Set A
Data Set B
Linear (Data Set A)
Linear (Data Set B)

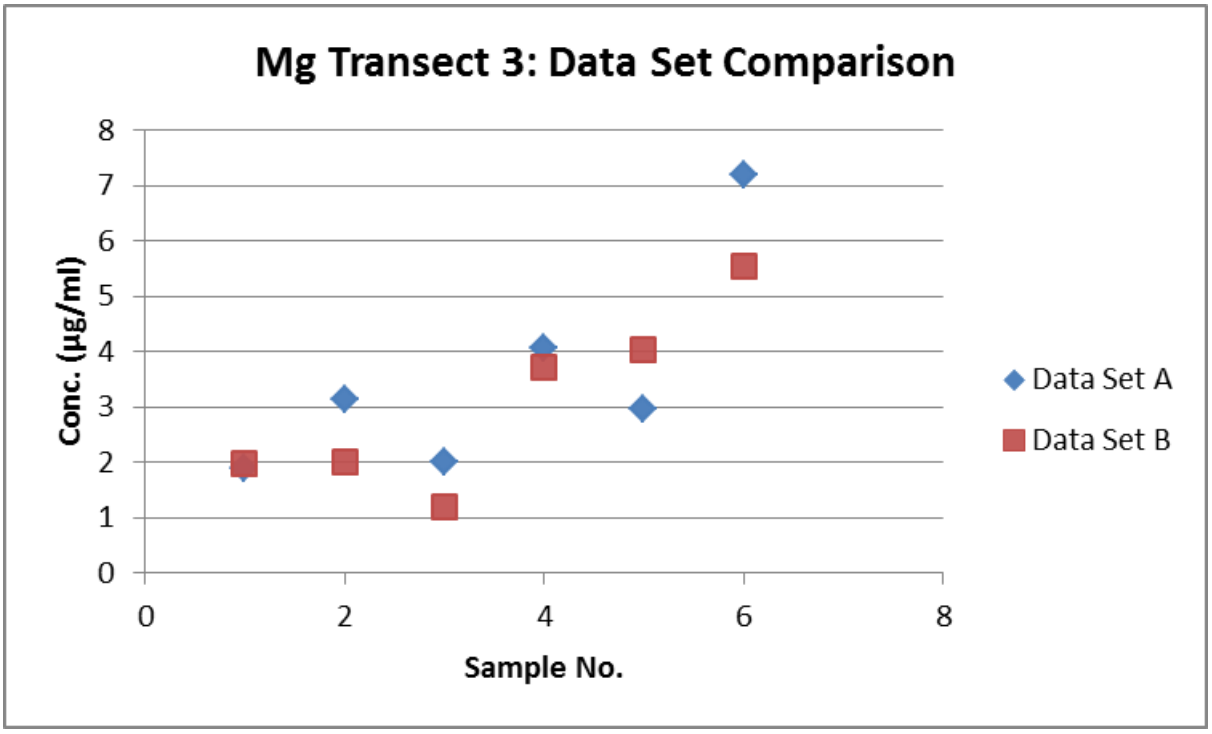

Ca Water: Data Set Comparison
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
Conc. (µg/ml)
0.5
1
1.5
2
2.5
3
3.5
Sample No. (+110)
Data Set A
Data Set B

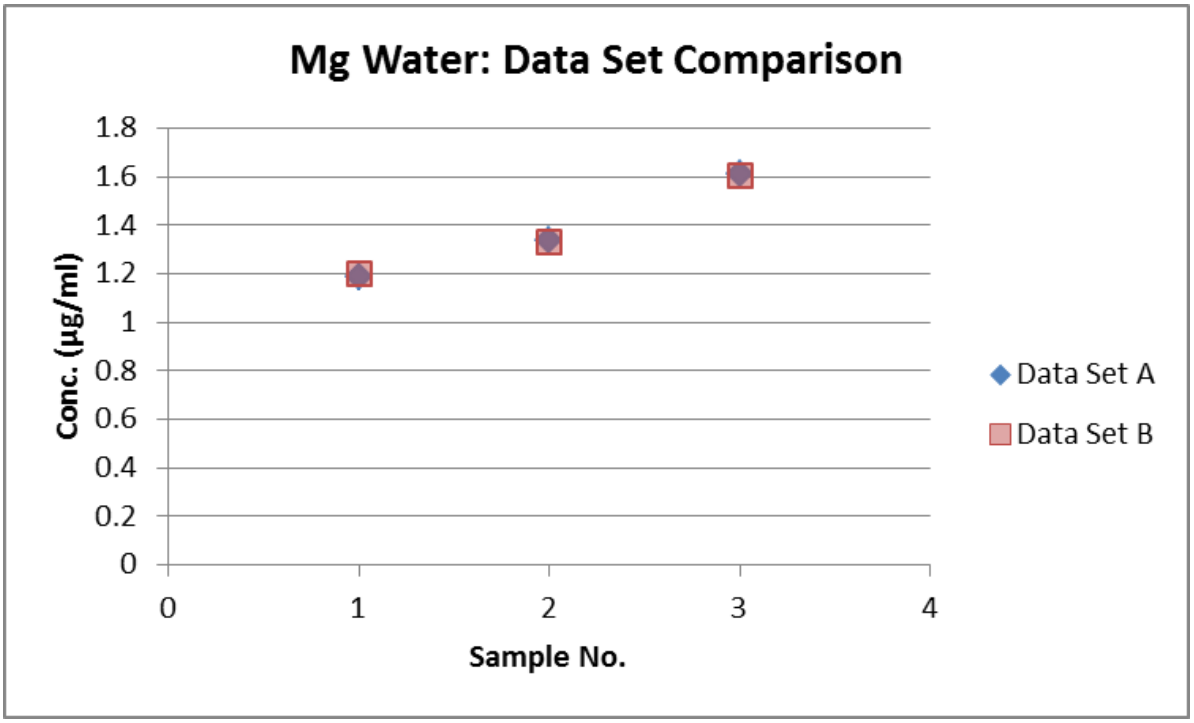

Mg Set A: Transect Comarison
Conc. (µg/ml)
Sample No.
0
1
2
3
4
5
6
7
8
0
5
10
T1
T2
T3
Water
Linear (T1)
Linear (T3)

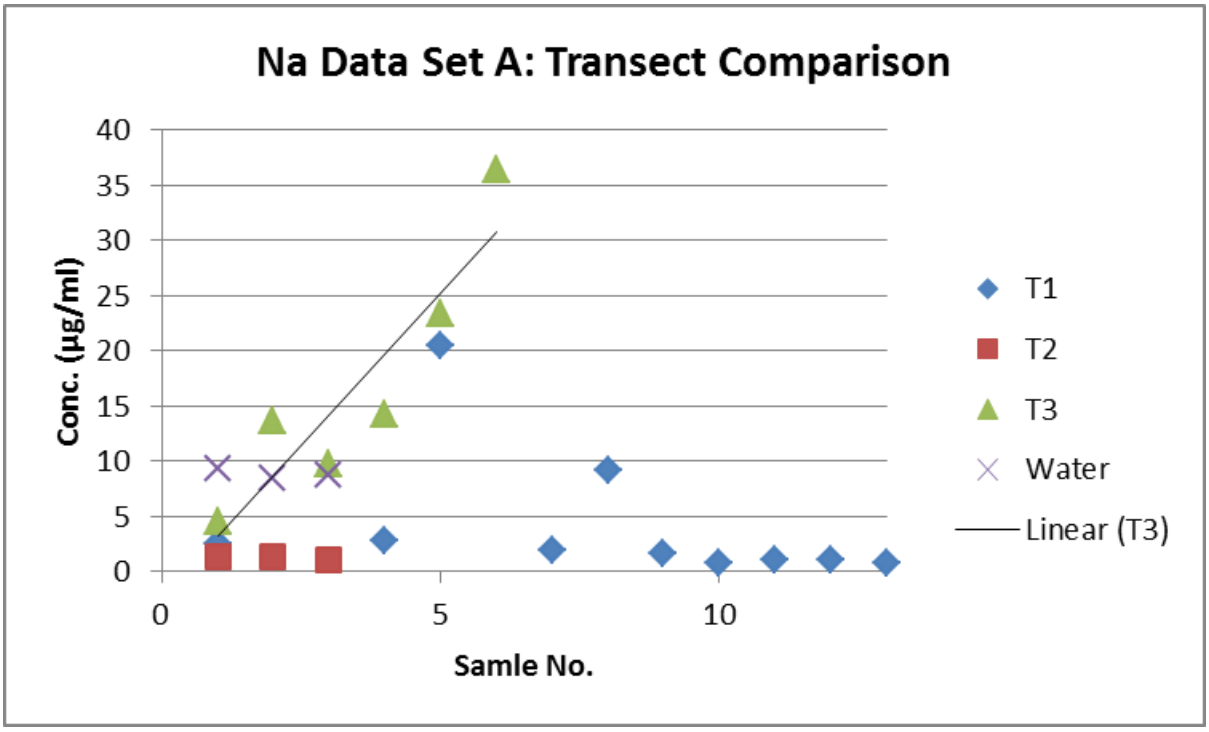

Mg Data Set B: Transect Comparison
Conc. (µg/ml)
Sample No.
0
1
2
3
4
5
6
0
5
10
T1
T2
T3
Water
Linear (T1)
Linear (T3)

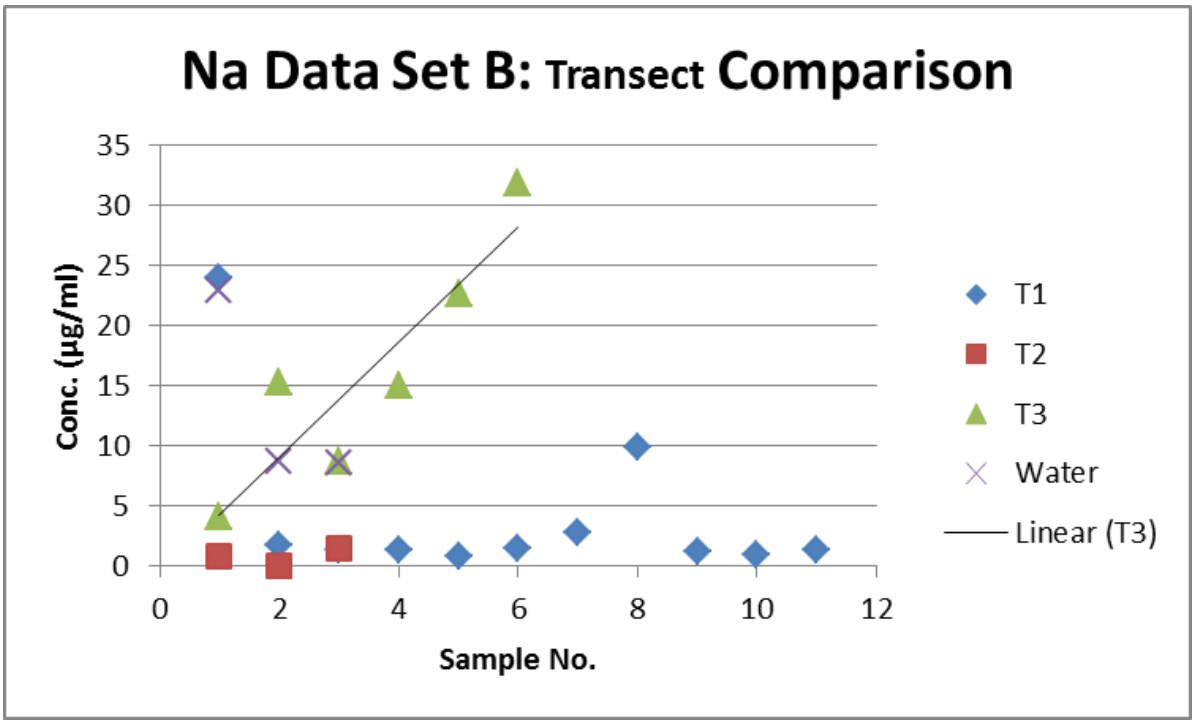

Mg Transect 1: Data Set Comparison
Conc. (µg/ml)
3
2.5
2
1.5
1
0.5
0
0
5
10
15
Sample No.
Data Set A
Data Set B

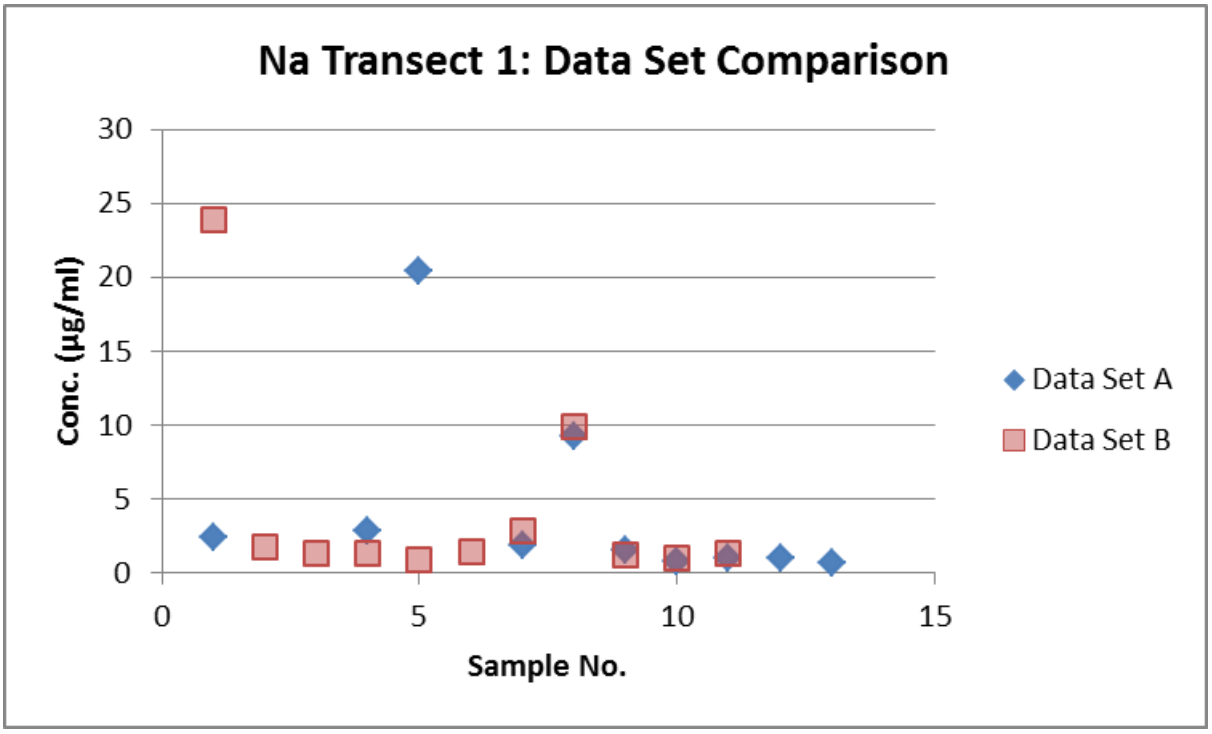

Mg Transect 2: Data Set Comparison
Conc. (µg/ml)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
Sample No.
Data Set A
Data Set B

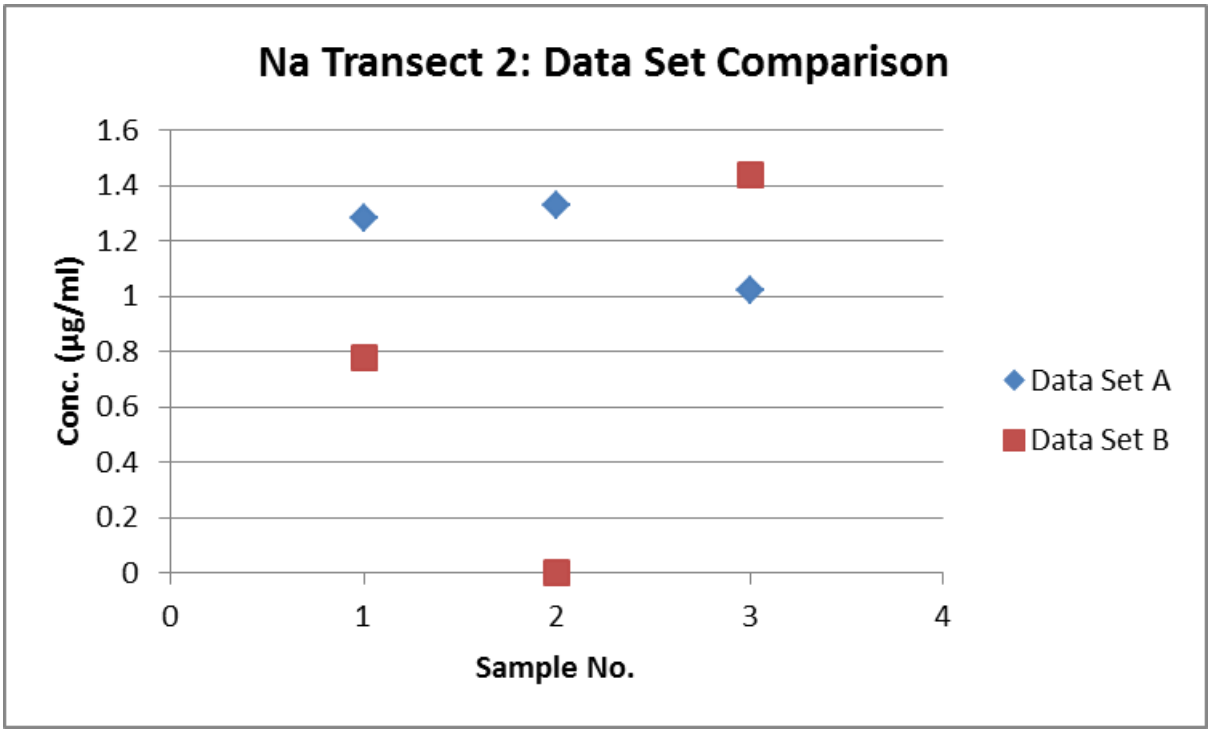

Mg Transect 3: Data Set Comparison
Conc. (µg/ml)
Sample No.
0
1
2
3
4
5
6
7
8
0
2
4
6
8
Data Set A
Data Set B

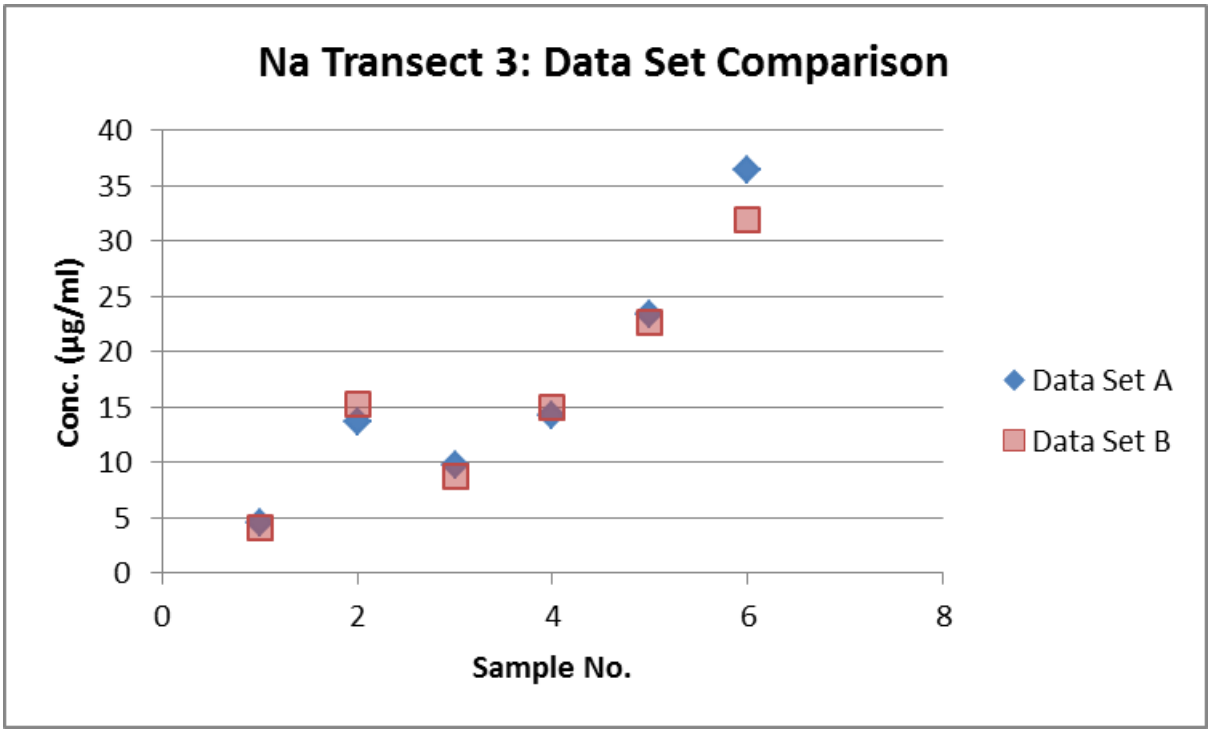

Mg Water: Data Set Comparison
Conc. (µg/ml)
Sample No.
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0
1
2
3
4
Data Set A
Data Set B

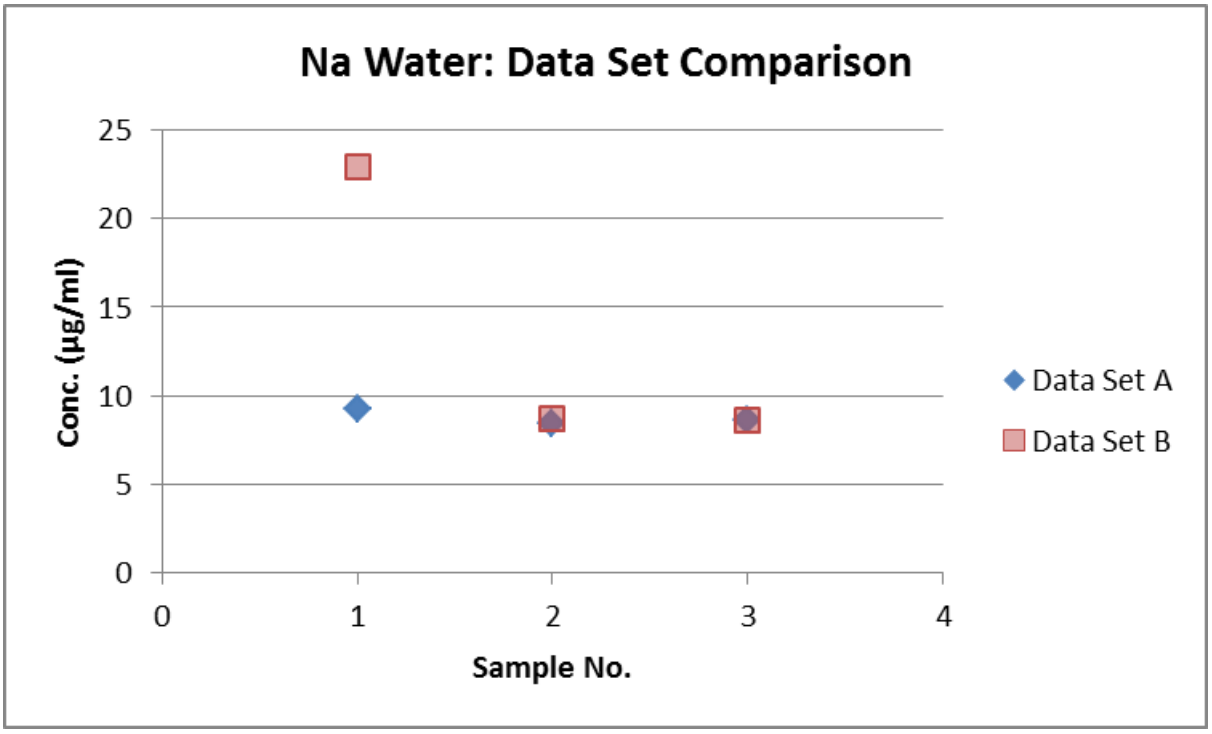

Na Data Set A: Transect Comparison
Conc. (µg/ml)
40
35
30
25
20
15
10
5
0
0
5
10
Samle No.
T1
T2
T3
Water
Linear (T3)

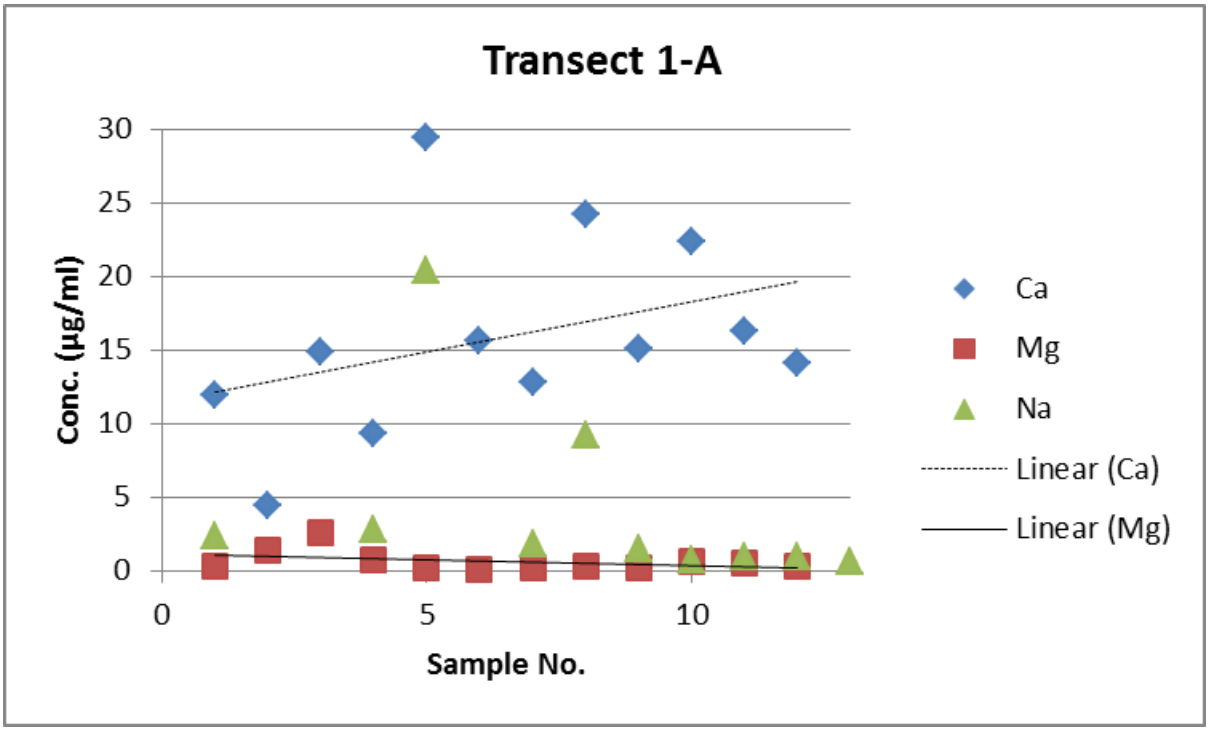

Na Data Set B: Transect Comparison
Conc. (µg/ml)
35
30
25
20
15
10
5
0
0
2
4
6
8
10
12
Sample No.
T1
T2
T3
Water
Linear (T3)

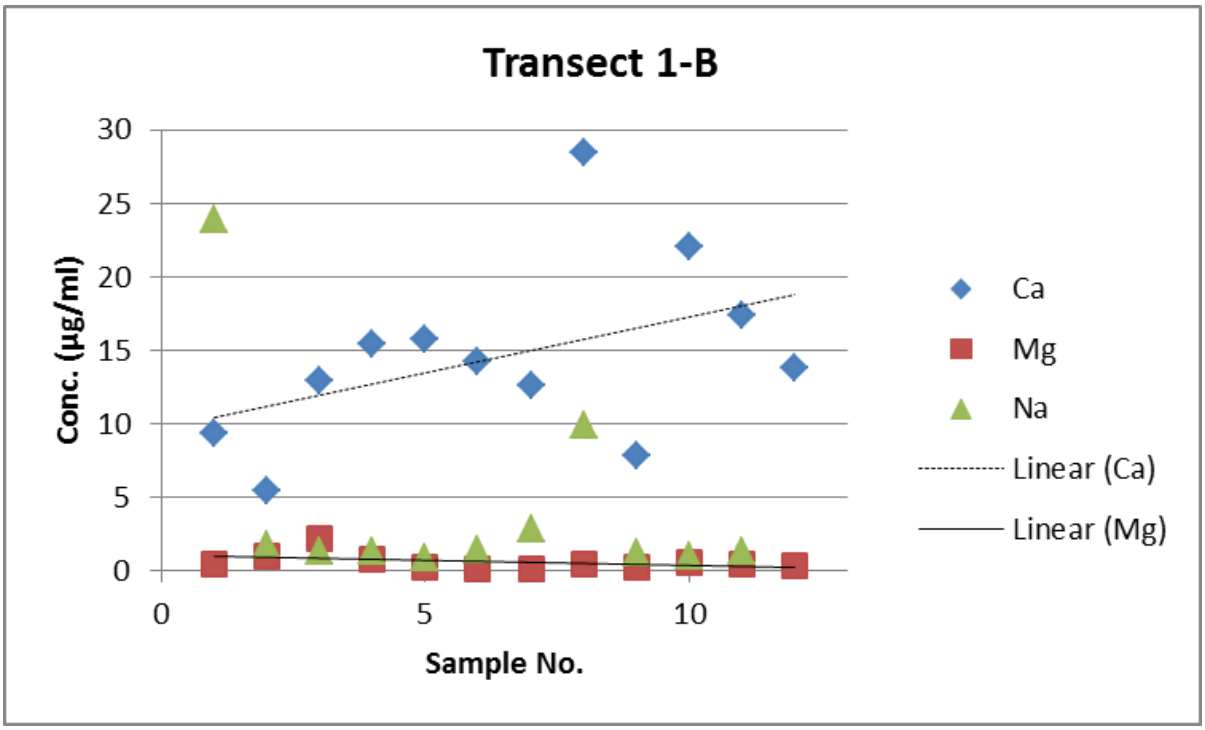

Na Transect 1: Data Set Comparison
Conc. (µg/ml)
30
25
20
15
10
5
0
0
5
10
15
Sample No.
Data Set A
Data Set B

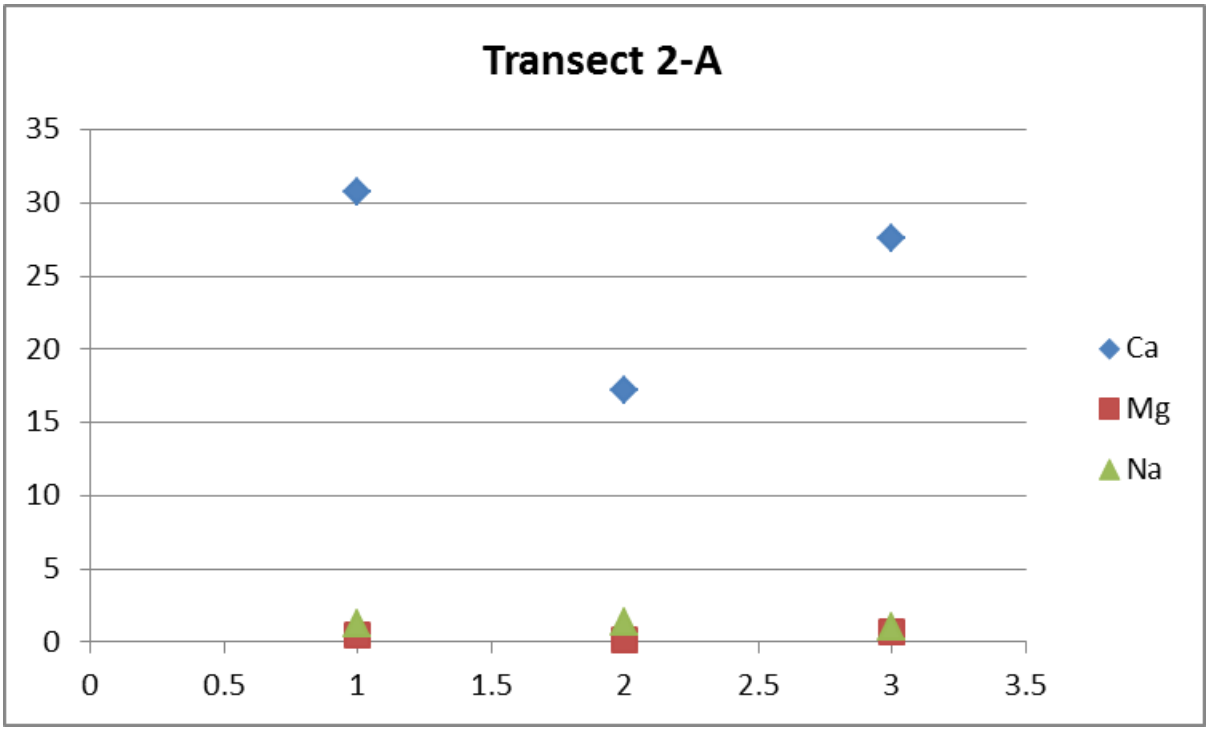

Na Transect 2: Data Set Comparison
Conc. (µg/ml)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
Sample No.
Data Set A
Data Set B

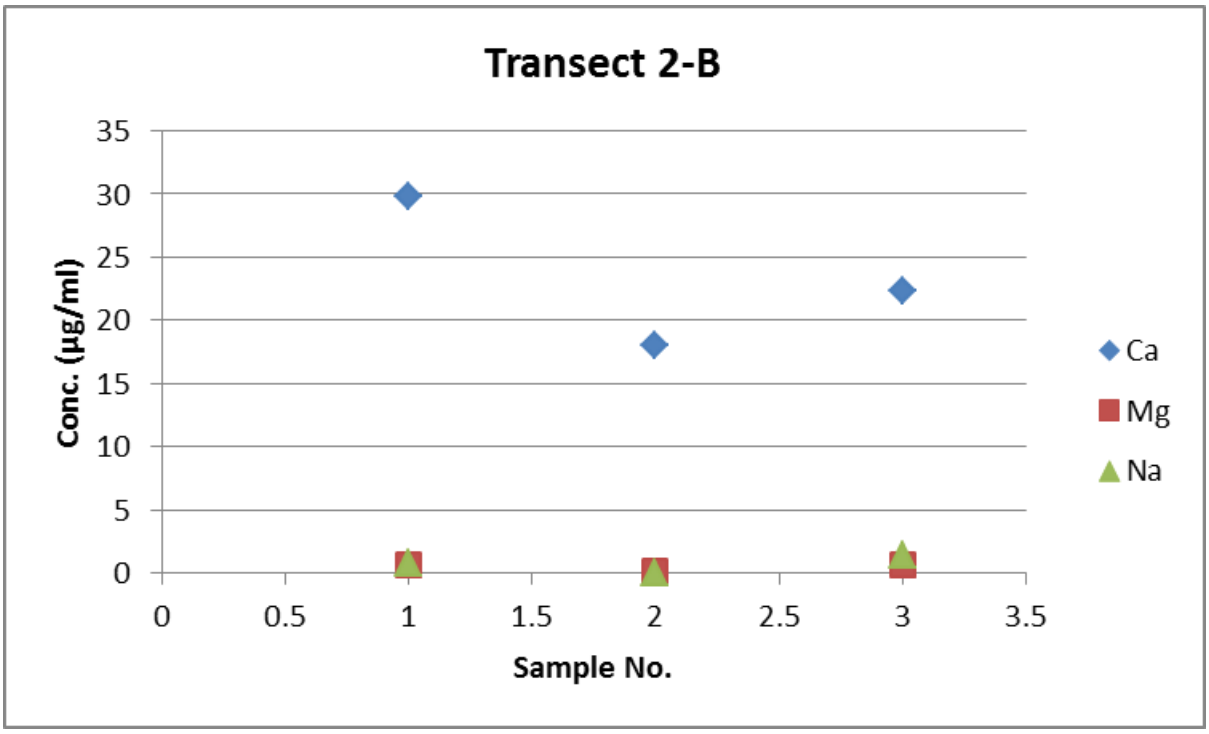

Na Transect 3: Data Set Comparison
Conc. (µg/ml)
40
35
30
25
20
15
10
5
0
0
2
4
6
8
Sample No.
Data Set A
Data Set B

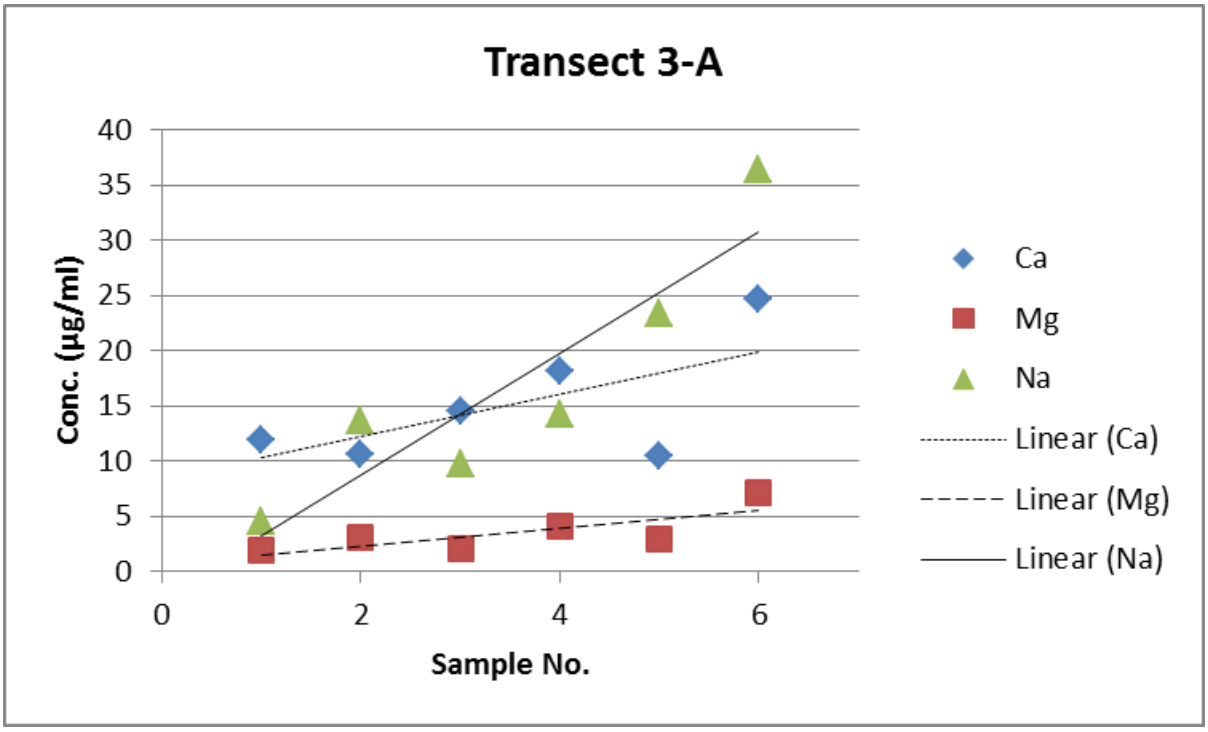

Na Water: Data Set Comparison
Conc. (µg/ml)
25
20
15
10
5
0
0
1
2
3
4
Sample No.
Data Set A
Data Set B

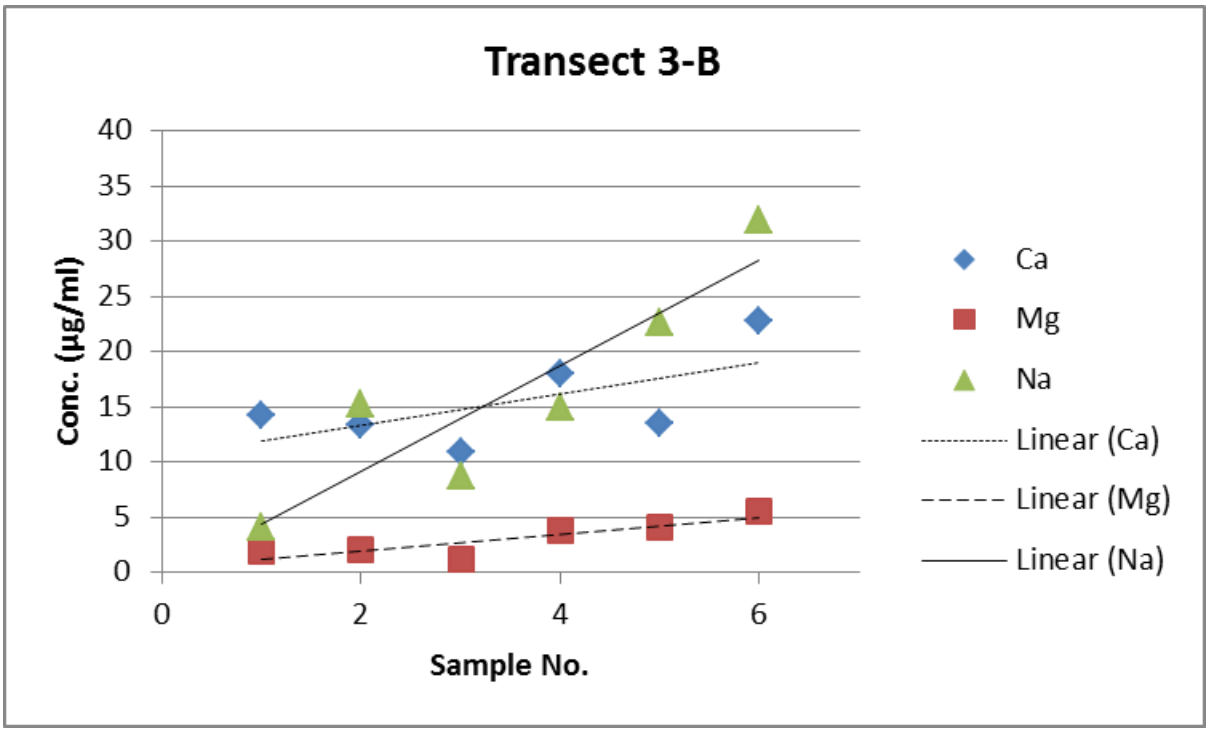

Transect 1-A
Conc. (µg/ml)
30
25
20
15
10
5
0
0
5
10
Sample No.
Ca
Mg
Na
Linear (Ca)
Linear (Mg)

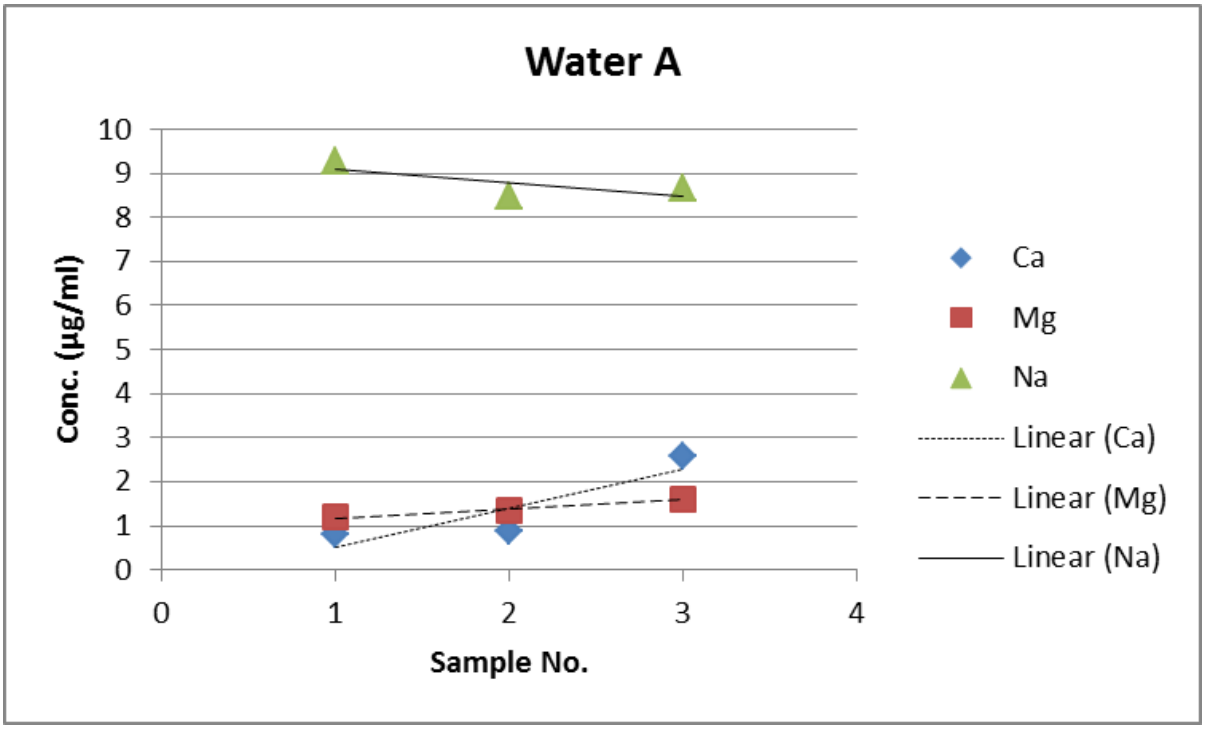

Transect 1-B
Conc. (µg/ml)
30
25
20
15
10
5
0
0
5
10
Sample No.
Ca
Mg
Na
Linear (Ca)
Linear (Mg)

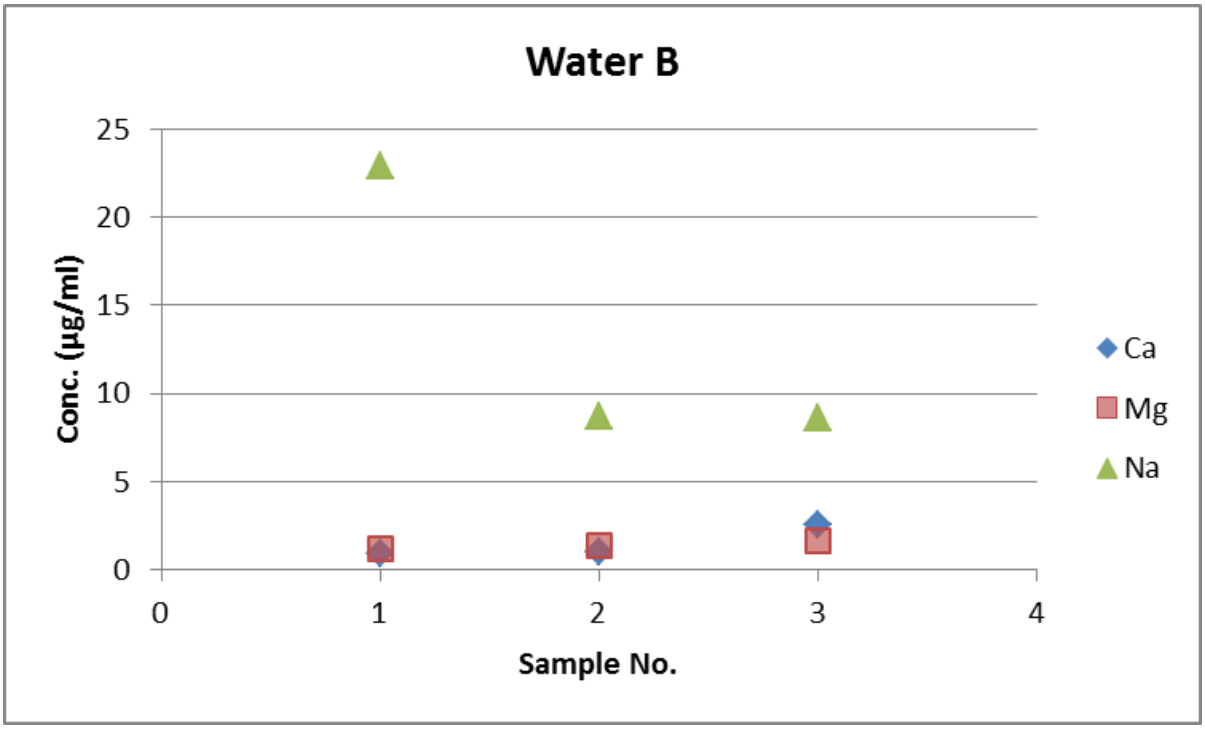

Transect 2-A
35
30
25
20
15
10
5
0
0
0.5
1
1.5
2
2.5
3
3.5
Ca
Mg
Na

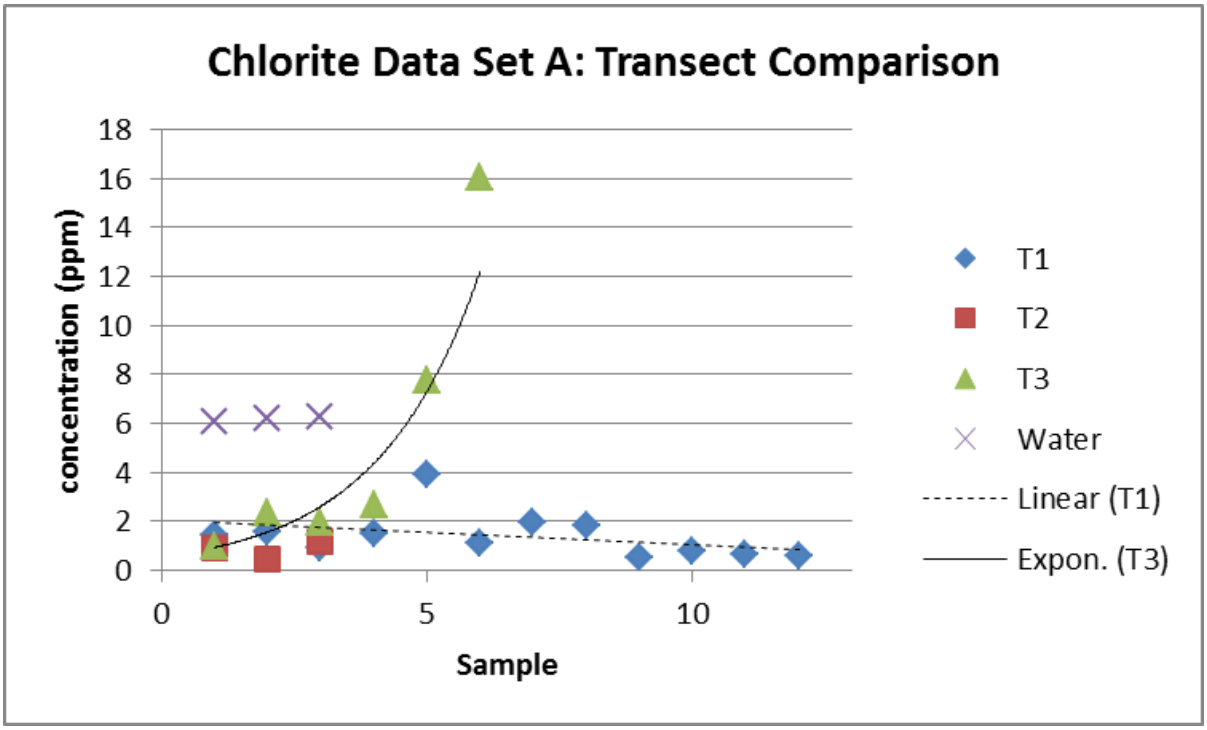

Transect 2-B
Conc. (µg/ml)
35
30
25
20
15
10
5
0
0
0.5
1
1.5
2
2.5
3
3.5
Sample No.
Ca
Mg
Na

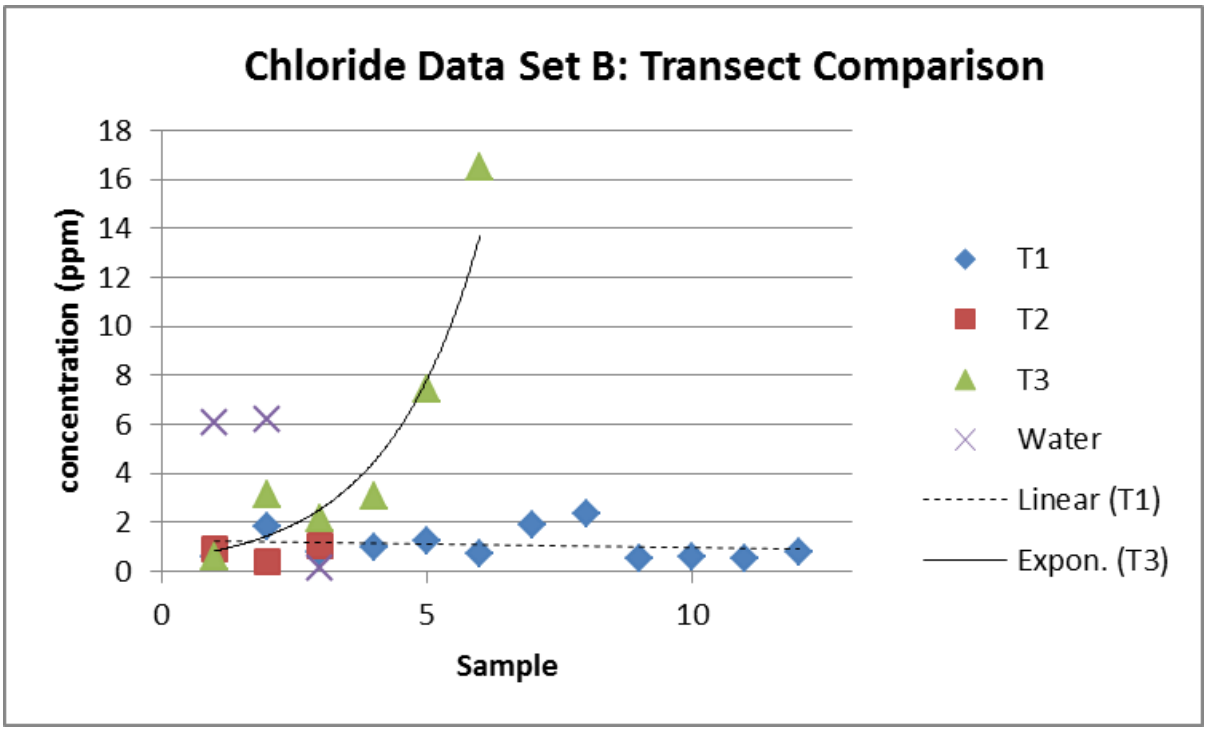

Transect 3-A
Conc. (µg/ml)
40
35
30
25
20
15
10
5
0
0
2
4
6
Sample No.
Ca
Mg
Na
Linear (Ca)
Linear (Mg)
Linear (Na)

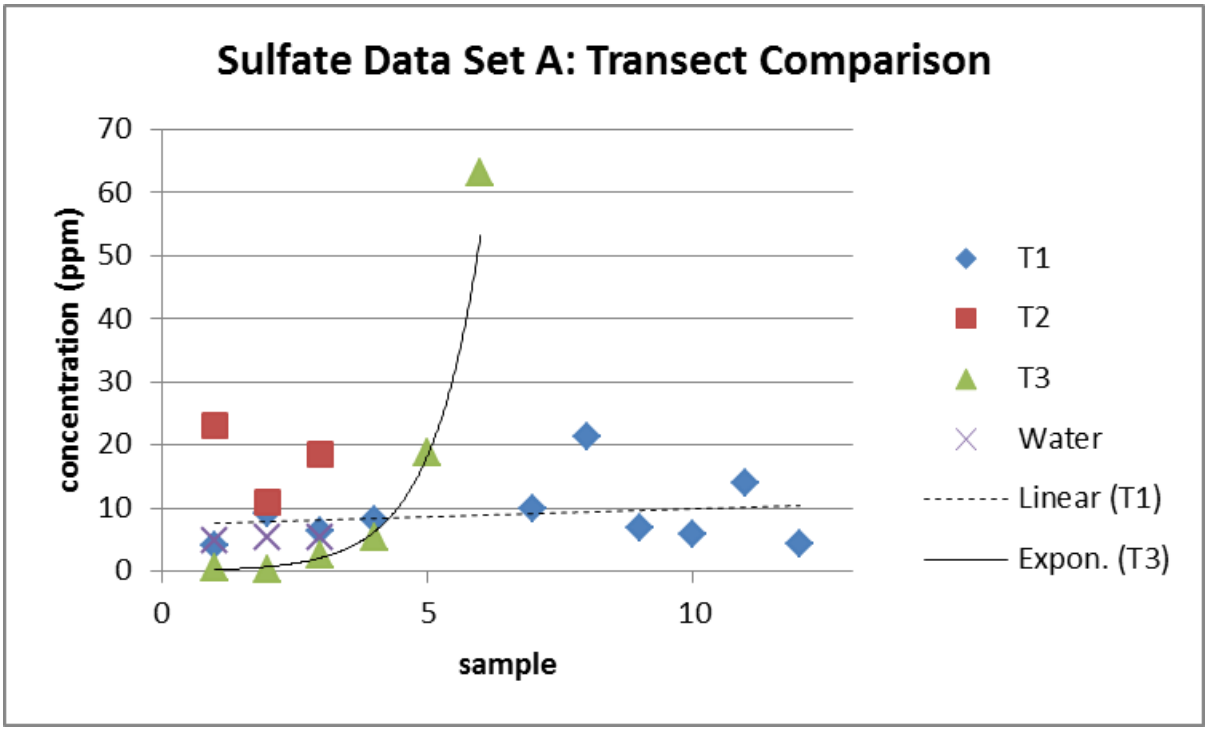

Transect 3-B
Conc. (µg/ml)
40
35
30
25
20
15
10
5
0
0
2
4
6
Sample No.
Ca
Mg
Na
Linear (Ca)
Linear (Mg)
Linear (Na)

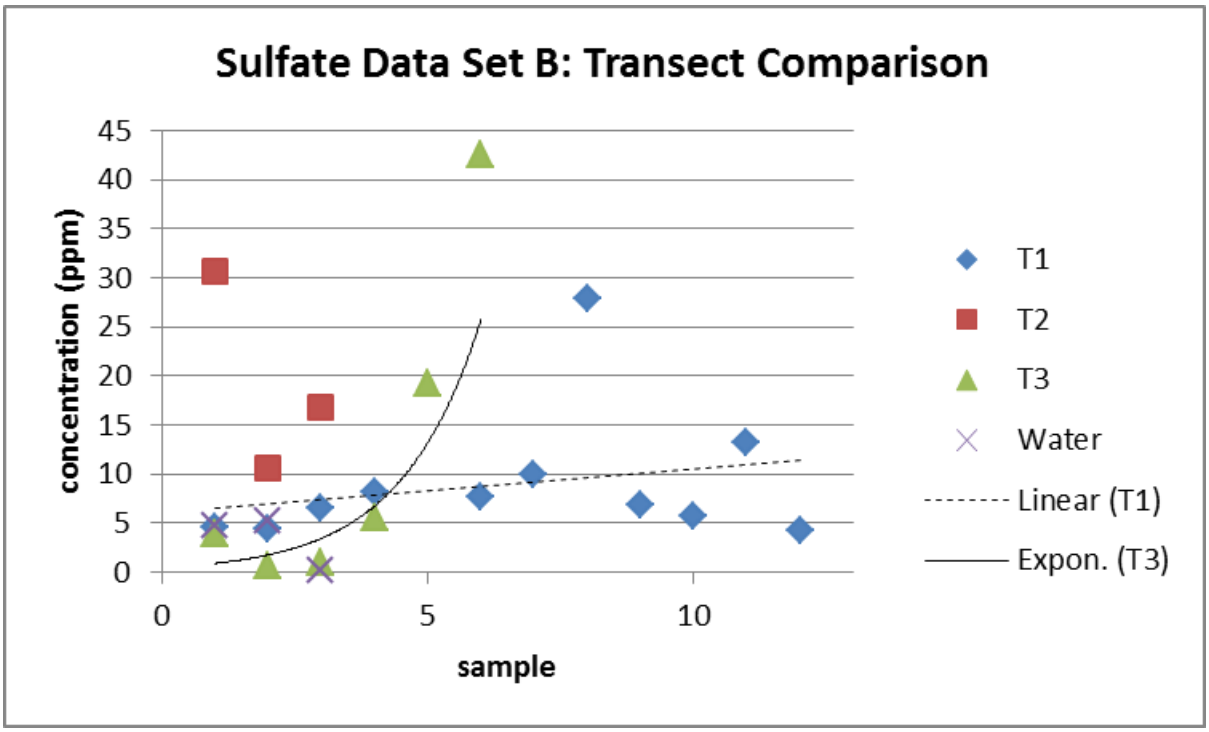

Water A
Conc. (µg/ml)
10
9
8
7
6
5
4
3
2
1
0
0
1
2
3
4
Sample No.
Ca
Mg
Na
Linear (Ca)
Linear (Mg)
Linear (Na)

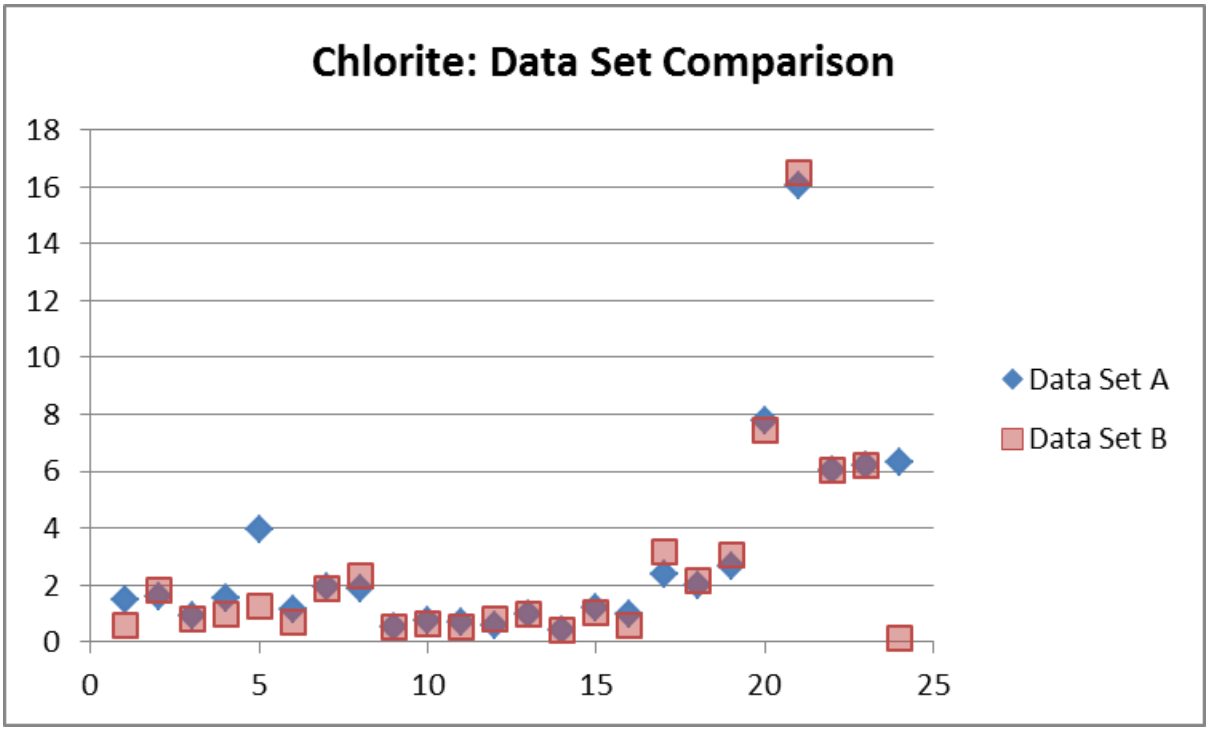

Water B
Conc. (µg/ml)
25
20
15
10
5
0
0
1
2
3
4
Sample No.
Ca
Mg
Na

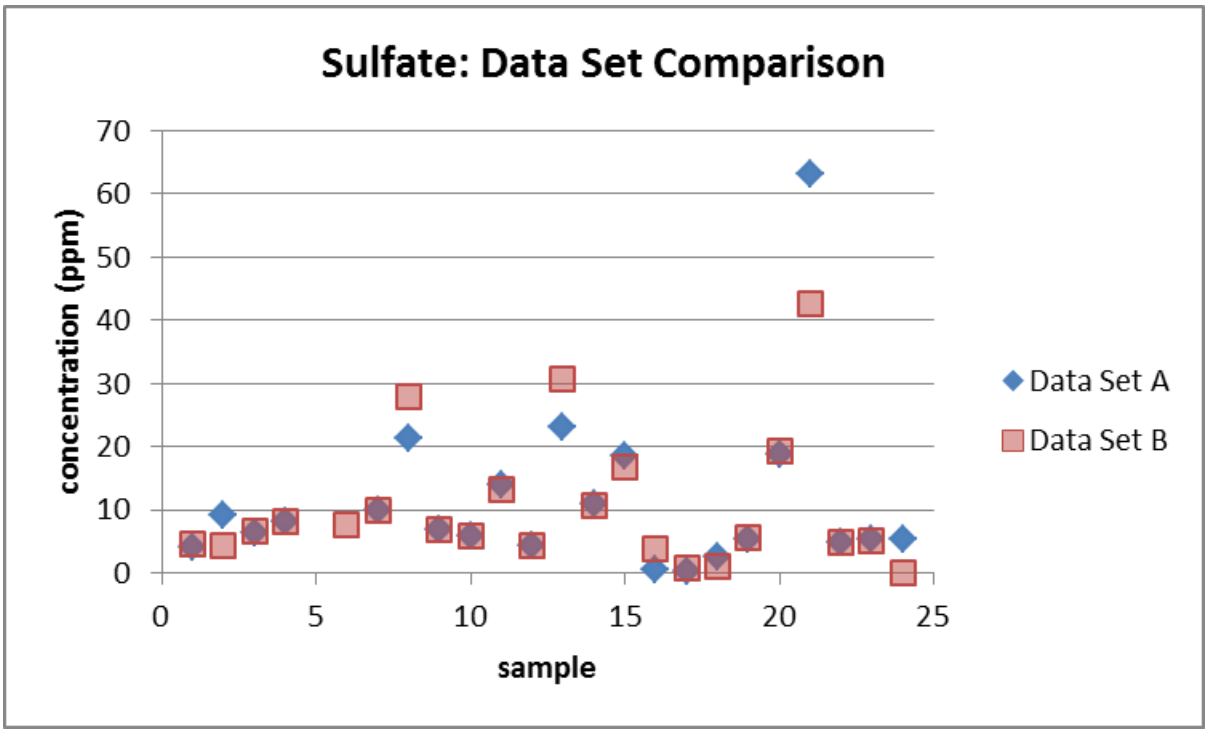

Chlorite Data Set A: Transect Comparison
concentration (ppm)
18
16
14
12
10
8
6
4
2
0
0
5
10
Sample
T1
T2
T3
Water
Linear (T1)
Expon. (T3)

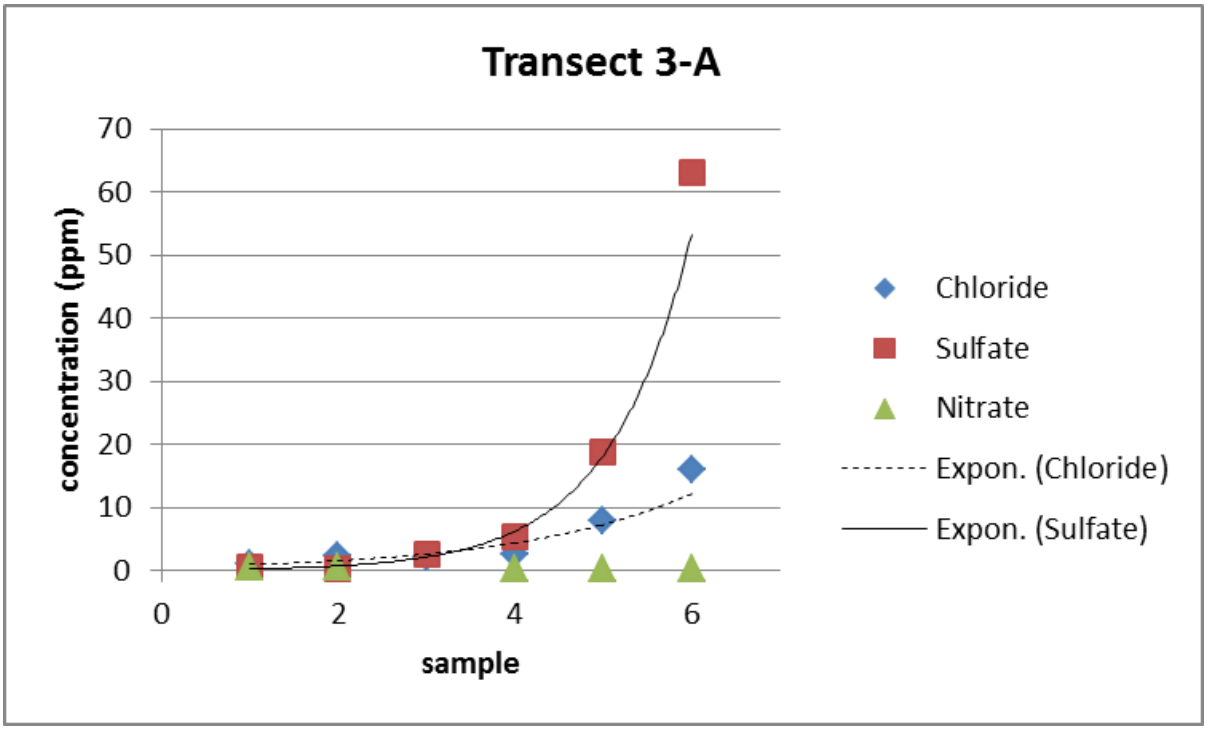

Chloride Data Set B: Transect Comparison
concentration (ppm)
18
16
14
12
10
8
6
4
2
0
0
5
10
Sample
T1
T2
T3
Water
Linear (T1)
Expon. (T3)

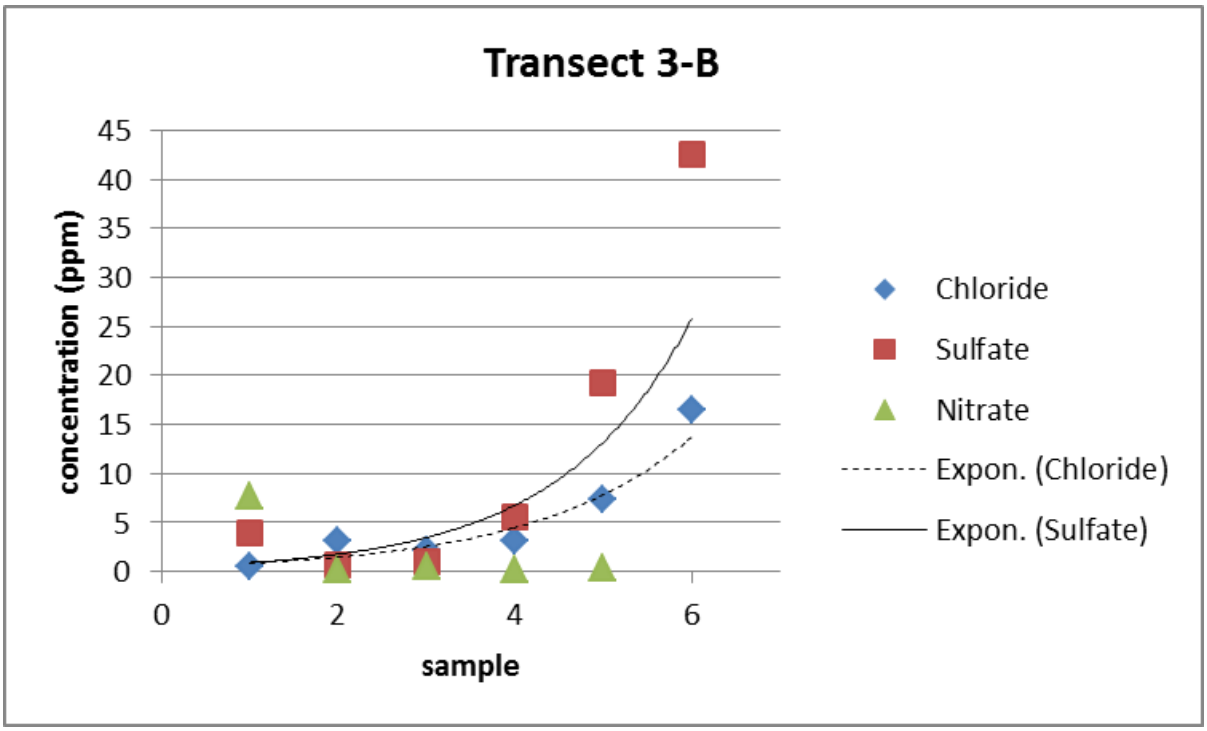

Sulfate Data Set A: Transect Comparison
concentration (ppm)
70
60
50
40
30
20
10
0
0
5
10
sample
T1
T2
T3
Water
Linear (T1)
Expon. (T3)

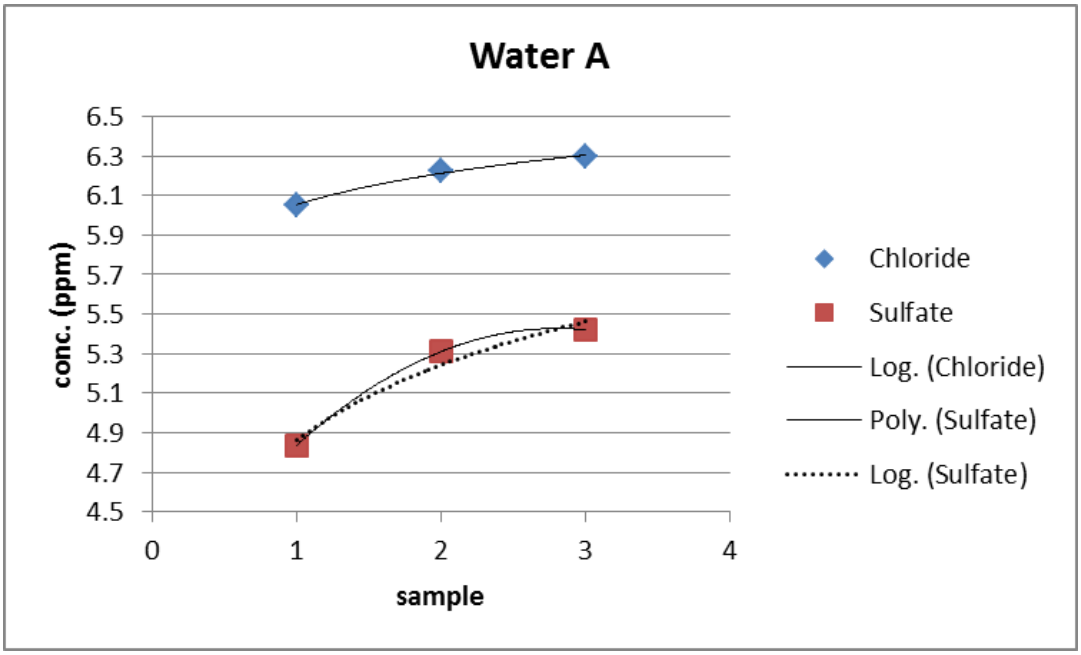

Sulfate Data Set B: Transect Comparison
concentration (ppm)
45
40
35
30
25
20
15
10
5
0
0
5
10
sample
T1
T2
T3
Water
Linear (T1)
Expon. (T3)


Chlorite: Data Set Comparison
18
16
14
12
10
8
6
4
2
0
0
5
10
15
20
25
Data Set A
Data Set B


Sulfate: Data Set Comparison
concentration (ppm)
70
60
50
40
30
20
10
0
0
5
10
15
20
25
sample
Data Set A
Data Set B


Transect 3-A
concentration (ppm)
70
60
50
40
30
20
10
0
0
2
4
6
sample
Chloride
Sulfate
Nitrate
Expon. (Chloride)
Expon. (Sulfate)


Transect 3-B
concentration (ppm)
45
40
35
30
25
20
15
10
5
0
0
2
4
6
sample
Chloride
Sulfate
Nitrate
Expon. (Chloride)
Expon. (Sulfate)



Lab Notes:

- AZ-313-B cation sample has suspended substance floating in water
- During solid waste weighing made sure to remove large roots and organic matter
- T1-S5-A; T1-S5-B; T1-S1-B measured without gloves
- Water samples: red = anion; yellow = cation
- Glass found in T1-S10
- Brushed off spoon and weighing tray between samples (not done for T1-S1)
- Samples added to tubes and shaken 9-9:45am Monday 12/05/12
- T1-S1 to T1-S9; T3-S5-B filtered with 0.45µm filter at 2-3pm Monday 12/05/12
- Rest of samples filtered 1-10am Tuesday 13/05/12
- T1-S2-A slightly yellow; re-filtered 13/05/12 but no color change
- T1-S5-A very yellow color; re-filtered 13/05/12 but no color change
- T3-S5-B dropped; ~12mL recovered (12/05/12); ~10mL of filtered sample water added (13/05/12)
- During cation testing: Sample 2 for Ca is T1-S2-B
- First cation standard was DI; first standard repeated
- All Na samples diluted by 10 (1g of sample added to 10g of DI); T1-S2-A diluted by 20; T1-S5-A diluted by 30; multiply concentration results by respective dilution number to find true concentration value
- Multiple recalibrations for cations:
    - Final Calibrations:
        - Ca: 50ppm; 15.85ppm; 5ppm
        - Mg:
        - Na: 6.85ppm; 11.285ppm; 22.00ppm
        - K: bulb burst