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Norske Skog Industrial Waste Effect On Water And Sediment Quality

Abstract:

Pulp and Paper Mills produce a variety of toxins and thus require careful disposal monitoring. The Kawerau hazardous waste site, located in Kawerau New Zealand, has been receiving waste from a neighboring paper mill for over 50 years. Monitoring the toxicity of this site, as stricter standards are imposed, is a necessity as it is located near a major body of water and a high groundwater level. In this project, soil and water samples were collected at various locations at the waste site. A modified Toxicity Characteristic Leaching Procedure (TCLP) procedure was used to test the leaching potential of the soil samples and AAS and HPIC were used to determine the concentration of certain Anions and Cations in the leachate and water samples. The results from this experiment indicate that some contamination from the Pulp and Paper mill is occurring, and while none of the observed chemicals are specifically regulated by the ministry of the environment, their presence serves as an indicator for other harmful toxins. Trends found in the graph suggest that certain areas of the waste site have much higher concentrations of pollutants than others and thus more thorough testing would prove more conclusive results.

Introduction:

Toxic landfill sites pose a variety of environmental health problems and thus require careful monitoring. Ensuring that harmful chemicals are contained within the landfill is the primary concern when managing a landfill site. Chemicals from waste sites are most commonly discharged into the environment through either surface runoff or groundwater leachate and thus water quality and soil leachate tests are excellent ways of monitoring and determining the effects and safety of a landfill site. Toxic landfills often face problems with leachate and groundwater discharge, so while this study specifically focuses on the Kawerau waste site it can

be applied in a global context for assessing landfill impact. Pulp and Paper mills discharge a variety of harmful chemicals as part of the milling process. While some amount of harmful waste is unavoidable, it is important to manage that waste and keep it at acceptable levels. A polluted groundwater source can make its way into surrounding water bodies which can, in turn, have a huge negative impact on the surrounding community by: destroying local ecosystems, causing health problems through bioaccumulation and biomagnification of food sources, infecting drinking water sources. Maintaining safe levels of potentially toxic chemicals is greatly important to maintaining the health of a region. Testing for major dissolved cations and anions in water samples along different locations in the waste disposal site will help determine how the quality of water is affected as it travels through the site. Testing soil samples for chemicals will help determine the effects the site will have on groundwater quality and will help determine what types of effects the site might have on the nearby Tarawera river.

Ensuring that waste sites maintain acceptable standards is important in maintaining equity for the local people that are affected by the hazardous waste. In this particular case, many standards have been ignored in the past and it is vital to ensure that moving forward, a certain level of monitoring is practiced. By testing and determining whether or not the Norske Skog is meeting acceptable waste standards this experiment could potentially produce results that may be useful in negotiations over lease extension as well as compensation for damages for the Iwi that have claim to the land.

The purpose of this project is to determine the impact of the industrial waste at the Norske Skog Paper Mill waste site on the nearby ponds by using a modified version of Toxicity

Characteristic Leaching Procedure (TCLP), a protocol developed by the United States Environmental Protection Agency. Atomic Absorption Spectroscopy (AAS) and High Pressure Ion Chromatography (HPIC) methodology will be used to determine cations and anions present in the water and leachate samples which will serve as indicators of contamination. Additionally, the project will help determine the potential groundwater effects due to leaching. I predict that the result from these experiments will yield data that indicate a high level of contamination from the paper mill.

Background info:

This project focuses on the waste disposal site of the Norske Skog Pulp and Paper Mill, formerly Tasman Pulp and Paper Company. In 1954, the New Zealand government passed the Tasman Pulp and Paper Mill enabling act by which allowed the Tasman Pulp and Paper Mill Company to take whatever steps they felt were necessary to build their industrial plant (Hikuroa, 2011). The New Zealand government was eager to jumpstart its economy and catch up with the rest of the first world and thus saw environmental damage as an acceptable sacrifice. Tasman Pulp and Paper co. seized an area of land in Kawerau due to the geothermal potential of the area which could subsidize electricity and heating costs. The Land is immensely important to the local Iwi who have used the thermal springs for hundreds of years. Despite efforts from the Kaitiaki, Tasman Pulp and Paper co. was given permission to build their paper mill and dispose of their waste in the surrounding area. A land lease was agreed upon which is soon to expire in 2013.

While the paper mill has been extremely successful over the years, comprising about 1% of New Zealand's GDP, it has been producing dioxins and many other harmful chemicals as part of the milling process (Hikuroa, 2011). To dispose of these chemicals the paper mill acquired the land around Lake Rotoitipaku, where it deposited many tons of toxic chemicals at levels exceeding modern standards. The Tasman Pulp and Paper Company act has since been repealed and the Mill is now operated by Norske Skog. Toxins have been buried at this site for over thirty years which has significantly impacted both the physical layout of the land and the health of the local Iwi. While standards have changed in recent years, and the waste that is being deposited is less toxic by several orders of magnitude, the site is still a cause for concern. Testing of this site will help the original Maori landowners in the process of acquiring compensation for the damages caused by the industrial waste and will help in the negotiation process as the lease on the land expires in the upcoming year.

The sampling sites were chosen because of their spatial orientation along the waste site. Additionally samples were taken at areas that have been used in recent years for waste disposal and would thus be the responsibility of Norske Skog. The Te Wai U Tuwharetoa spring is a sacred spring that feeds fresh clean water into the waste site. This sample serves as a control and should yield very low dissolved ion readings.

Method:

The procedure for this project surrounds testing of water and sediment samples that were collected on Feb 10th 2012. Water samples were collected from three different locations along the waste site. One sample was taken from the Te Wai U Tuwharetoa spring which acts as

the water source for the nearby ponds; this sample will serve as the control. The other two samples were taken from the two nearby ponds that are connected by a high groundwater surface. These locations were selected due to their spatial separation at the sight.



Aerial view of the Norske Skog waste site. The Yellow arrows point to the two water sampling sites and the three lines represent the three soil sampling transects. Red is T1, Green is T2, Purple is T3.

Water samples were taken in 1L containers. Sampling containers were rinsed three times by the source water to ensure pure samples. Each sample was tested immediately for pH, Temperature, Dissolved Oxygen and Conductivity. After initial testing, each sample was filtered using a syringe and a 0.45 μm membrane filter to remove suspended solids in the sample. These samples were stored in a closed container for several months until laboratory testing could begin.

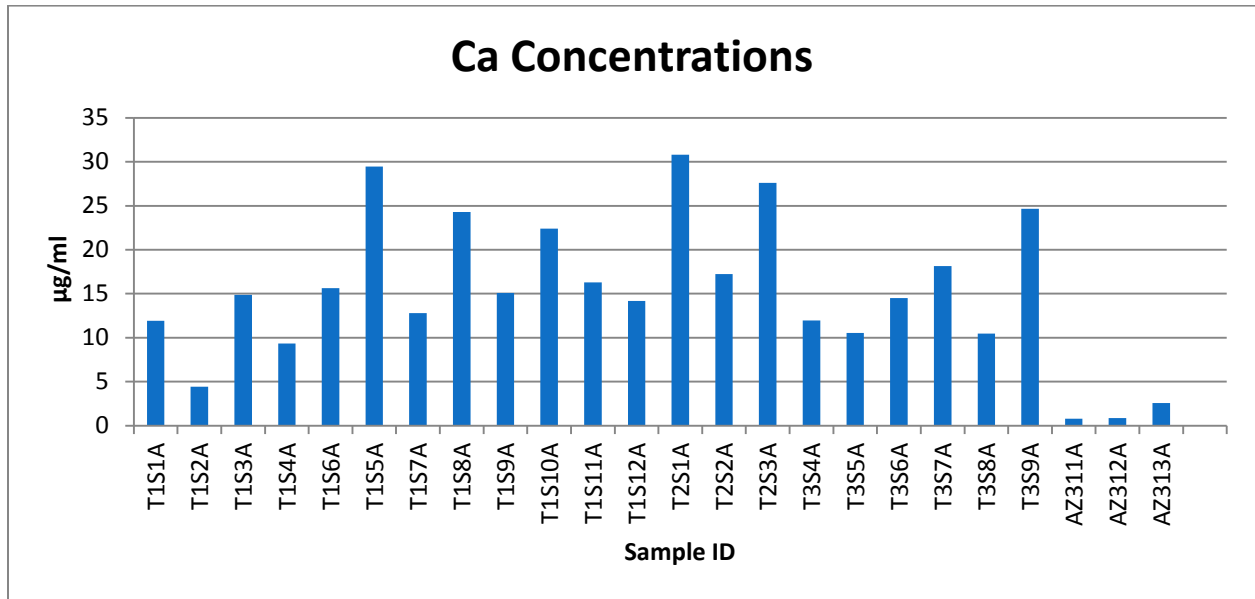
The second part of the project involves leachate testing of soil samples. Soil samples were collected along three different transects on the western bank of the Rototipaku. 50-200g Samples were collected at 2m intervals along the transects and were stored in sealed plastic bags. Physical observations of these samples were also made in the field. The samples were stored in a closed container for several months until testing could commence.

In the lab, an adapted version of the TCLP protocol was used to determine the levels of specific cations and anions that were present in the soil. Approximately 4g (+/- 0.1g) of each sample was added to two different centrifuge tubes as one would be used to test for anions and the other would be used for cation testing; this step was repeated for each sample so there would be two replicates per sample. 40ml of DI water was then added to each centrifuge tube, which was then mixed vigorously for 5 minutes. The tubes were then left to settle for 4-5 hours, and were then decanted and filtered through 0.45µm filters so to attain a clear sample devoid of most suspended solids.

The filtered sediment samples, along with the water samples, were then tested for concentrations of Na, Mg, and Ca using AAS (Atomic Absorption Spectrometry). Some samples had to be diluted as they exceeded the base sample concentrations that were used in AAS as a reference to determine concentrations of samples. To determine the anion concentrations, IC (Ion Chromatography) protocol was used to measure conductivity. Based on conductivity readings over time of each sample it was possible to determine the concentrations of different anions. Using the data gathered from AAS and IC, it was possible to make determinations about the level of contamination at the site by comparing the concentrations to certain standards.

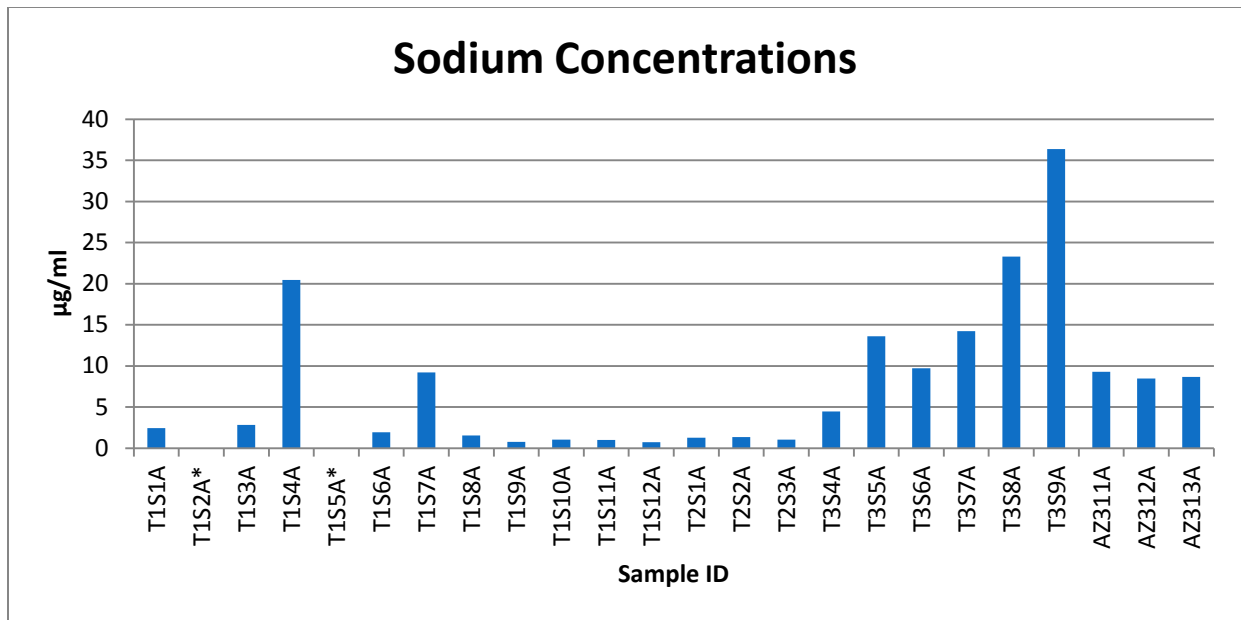
Results:

Cation concentrations:



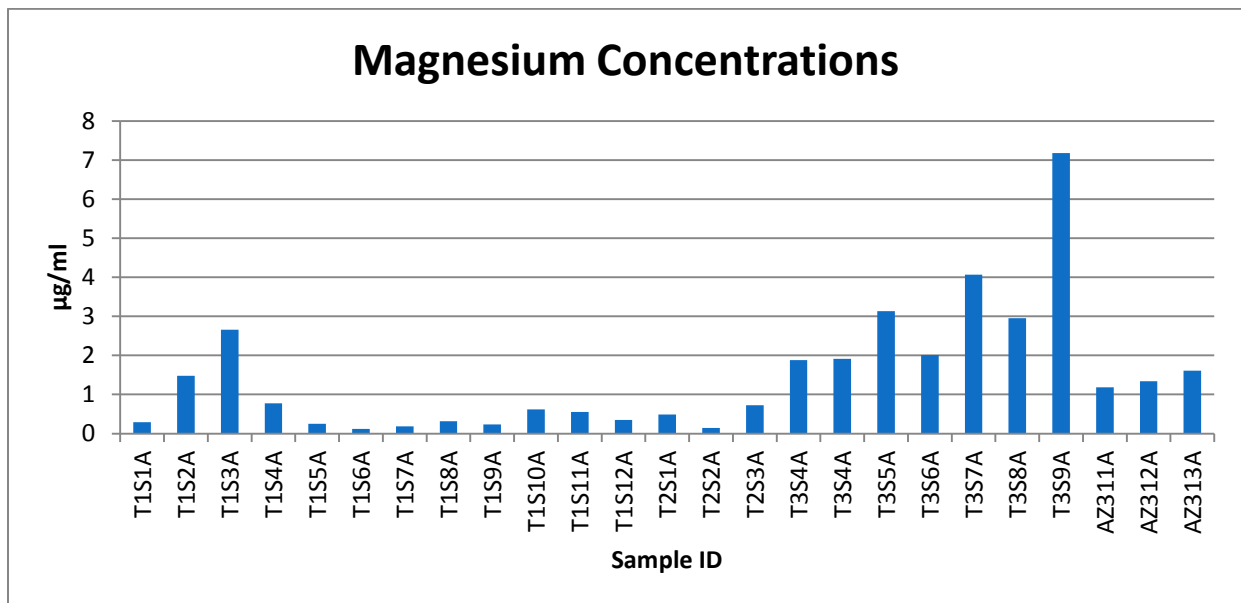
Graph 1: Calcium Concentration

The average calcium concentration for the soil leachate samples was calculated to be 16.98, with a standard of 7.05. The average concentration of the water samples is 1.41. While there doesn't not appear to be much of a trend along each transect, it should be noted that the leachate concentration is considerably higher than the water sample concentration.



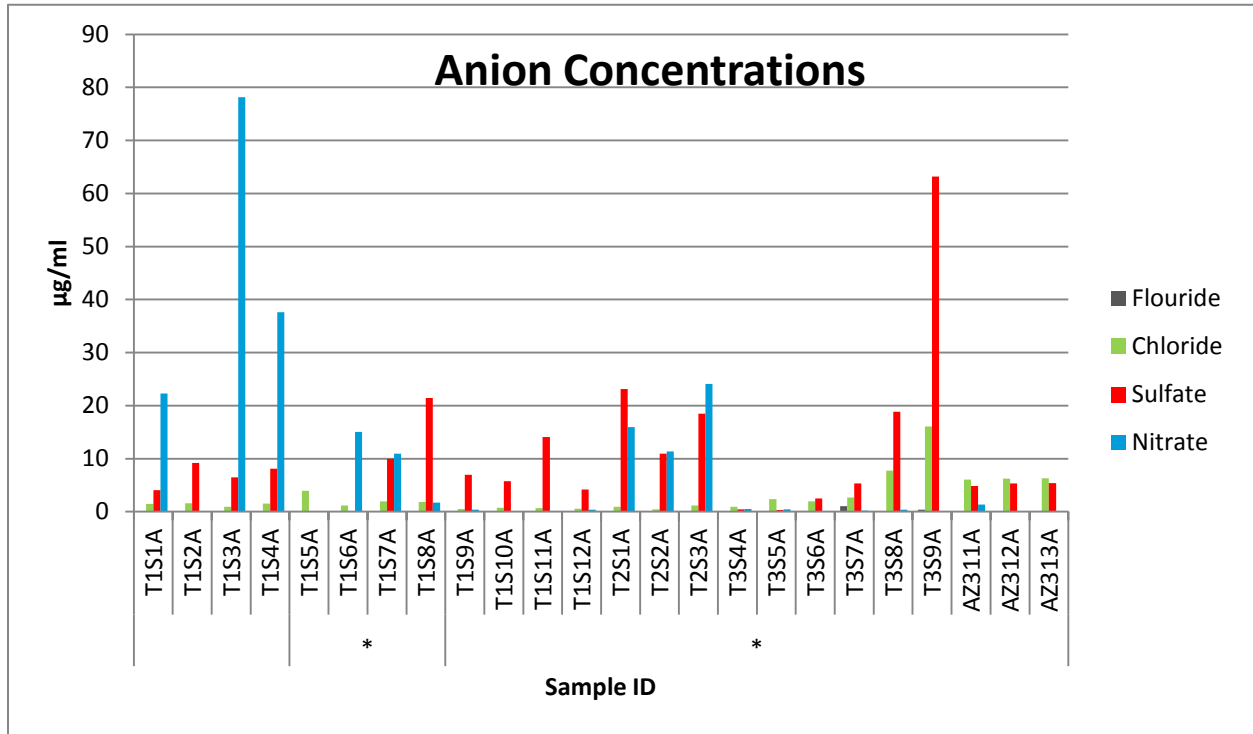
Graph 2: Sodium Concentration

T1S2A and T1S5A were removed from the graph because there were substantially higher than the other measurements. T1S2A recorded a concentration of 364.92 and T1S5A recorded a concentration of 503.22. The average Sodium concentration including these two outliers was calculated to be 48.36 with a very large standard deviation of 130.42.



Graph 3: Magnesium Concentrations

The average magnesium concentration in the leachate samples was calculated to be 1.47, with a standard deviation of 1.72. The average for the water samples is 1.38. There appears to be pretty low concentrations along transect 1 and then a steady increase along transect two and three.



Graph 4: Anion Concentrations

Nitrate had an average concentration of 12.27 with a standard deviation of 19.74. Chloride had an average concentration of 2.91 with a standard deviation of 3.51. Sulfate had an average concentration of 11.32 with a standard deviation of 13.29.

Table 4. Varying Amount of Solid Experiments: Cation Concentrations.

Sample ID	[Ca] µg/mL	[Mg] µg/mL	[K] µg/mL	[Zn] µg/mL
CH23 (2g)	2.768	1.912	3.162	0.007
CH25 (4g)	11.710	6.123	4.877	0.016
CH27 (8g)	12.859	5.264	4.140	0.004
CH24 (2g)	-0.889	0.569	2.127	0.009
CH26 (4g)	0.960	1.283	2.379	0.011
CH28 (8g)	50.205	HIGH	11.173	0.006

Note: Two different pH levels were used, 3.23 and 5.53. The first three listed samples, CH23, 25, 27 were at pH 3.23 and samples CH 24, 26, 28 were at pH 5.53.

Results done from a previous study. See Howell.

Discussion:

The results produced by this experiment, while limited due to time constraints and resources, can still be used to make several conclusions and inferences. The compounds and elements that were tested for in this project are all naturally occurring, however, the results indicate that these chemicals are found in higher than baseline concentrations. There are also several trends that can be seen on the graphs. Sodium, Magnesium and Chloride all appear to follow a similar trend. All three components appear to have a higher concentration at the beginning of transect 1 and seem to level off toward the middle of transect one and through transect 2; this makes sense as this sampling area was more vegetated than the areas that yielded higher concentrations. There also appears to be a steep increase in concentration at transect 3 where the soil was described to be 'pulpy' and appeared to have been deposited more recently. If future studies are to be done, more samples should be collected from areas that fit this description.

While one of the main objectives of this project was to compare the results to findings that have been recorded in previous years, it was quite difficult to achieve with the limited data that was accessible. Due to time constraints it was not possible to perform leachate tests at varying pH, settling time, and soil sample mass as had been done in previous years. Because pH was not monitored, it was very difficult to compare the findings in this procedure to results found in previous years. The table below compares regulation standards for leachate concentrations to values determined from this experiment.

	ANZECC (µg/ml)	NSW-EPA (µg/ml)	NZS 9201 (µg/ml)	Drinking Water Std (µg/ml)	experimental conc. (ave)	experimental conc. (max)
Chloride	–	–	–	200	2.91	16.0469
Mg+Ca (Hardness)	–	–	–	250	18.45	37.97
Flouride	–	150	30	1.5	–	–
Nitrate	0.700	–	–	50	12.27	78.1385
Sodium	–	–	–	200	48.36	503.22
Sulphate	–	–	–	250	11.32	63.1953

Table 2: Data taken from the Ministry of the Environment report on class A landfills

Most of the chemicals that were tested for are not specifically regulated by the Ministry of the environment in regards to leaching concentrations. Drinking water standard concentrations are included in the table to provide a reference for concentration values as most of the chemicals do not have a regulatory leachate standard to compare to. Nitrate and Sodium are the most prominent contaminants observed in the table. The max concentration for both Nitrate and Sodium exceed the drinking water standard by a wide margin. Sodium Hydroxide is commonly used in conjunction with dioxins for bleaching as part of the paper production process (World Bank Group, 1998). The high level of sodium found at certain location may indicate the presence of dioxins.

One thing to be noted is the high variance in concentrations between different samples. Every element that was tested for, with the exception of Ca, had a standard deviation that exceeded the mean concentration value of the data set. This indicates that a couple samples

contained much higher concentration than the rest of the data set. This is seen most prominently in the sodium results. Two samples yielded concentrations that far exceeded any of the other samples by several orders of magnitude. It was noted that these two particular leachate samples had a yellowish discoloration. A lot of the solid samples were observed to have different texture and were for the most part non-homogenous, so it is quite possible that certain parts of the sample had higher contamination levels than others. It is possible that there was cross contamination of the samples at some point during procedure, or there was a machine malfunction. It is impossible to make a determination either way without further testing. In the future, more replicates would help eliminate anomalies.

Ultimately, more extensive studies need to be done at this site to make more definitive conclusions. Carrying out a complete TCLP would be the best way to achieve more thorough results that could ultimately be used as an assessment tool for the Ministry of the Environment. Additionally, testing should be done for associated harmful organics and heavy metals that are often disposed of along with the elements that were tested for as part of the milling process. While TCLP tests are useful in assessing what types of chemicals are present in a waste site, they are not meant to replicate a natural leaching scenario. To fully determine the effects the sight might have on the surrounding groundwater, testing should be done on ground water samples in addition to a leachate test that is meant to replicate a natural groundwater leaching scenario.

Conclusion:

Ultimately the objective of this project was to assess what contaminants may be present at the Kawerau waste sight, and provide guidance for future research at this sight. An adapted TCLP procedure was performed and leachate samples and water samples were tested for several cations and anions. The Results conclude that contamination from the Pulp and Paper mill is occurring. Trends found in the graph suggest that certain areas of the waste sight have much higher concentrations of pollutants than others and thus more thorough testing would prove more conclusive results. Future leachate tests on more regulated associated chemicals should be done on samples away from vegetation and at fresh dumping sights.

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Appendix:

Cations

Calcium	Sample ID			µg/ml
	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
	T1S6A	15.646	2.14	0.3347
	T1S5A	29.461	6.7	0.5564
	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

Sodium	Sample ID				µg/ml
	T1S1A	0.243	11.91	0.0112	2.43
	T1S2A*	18.157	0.96	0.9226	363.14
	T1S3A	0.282	15.76	0.013	2.82
	T1S4A	2.047	0.79	0.0951	20.47
	T1S5A*	16.774	1.21	0.8455	503.22
	T1S6A	0.191	18.37	0.0088	1.91
	T1S7A	0.92	15.35	0.0425	9.2
	T1S8A	0.155	7.78	0.0071	1.55
	T1S9A	0.076	HIGH	0.0035	0.76
	T1S10A	0.102	HIGH	0.0047	1.02
	T1S11A	0.1	14.95	0.0046	1
	T1S12A	0.072	HIGH	0.0033	0.72
	T2S1A	0.128	HIGH	0.0059	1.28
	T2S2A	0.133	5.73	0.0061	1.33
	T2S3A	0.102	HIGH	0.0047	1.02
	T3S4A	0.444	4.01	0.0204	4.44
	T3S5A	1.362	2.42	0.063	13.62
	T3S6A	0.971	6.32	0.0448	9.71
	T3S7A	1.421	1.01	0.0658	14.21
	T3S8A	2.33	0.29	0.1083	23.3
	T3S9A	3.635	1.02	0.1702	36.35
	AZ311A	0.927	4.71	0.0428	9.27
	AZ312A	0.847	1.23	0.0391	8.47
	AZ313A	0.865	2.4	0.0399	8.65

Magnesium	Sample ID			µg/ml
	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
	T3S4A	1.91	2.63	0.1018
	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

Anions

Compound (ppm)		Flouride	Chloride	Nitrite	Sulfate	Bromide	Nitrate	Phosphate
	T1S1A		1.4521		4.0775		22.2984	
	T1S2A		1.5708		9.1745			
	T1S3A		0.9295		6.4958		78.1385	
	T1S4A		1.5091		8.128		37.6012	53.9247
*	T1S5A		3.9306					
	T1S6A		1.1435				15.0333	
	T1S7A		1.9534		9.9551		10.9682	15.4417
	T1S8A		1.8515		21.4312		1.7078	
*	T1S9A	0.1195	0.5317		6.9365	0.1616	0.414	
	T1S10A		0.7689		5.7825	1.0189		
	T1S11A	0.1025	0.6726		14.0756			
	T1S12A	0.08	0.5709		4.2162		0.3787	
	T2S1A		0.9526		23.1251		15.9231	

	T2S2A	0.1136	0.4362		10.9605		11.3709	
	T2S3A	0.08	1.1907		18.5129		24.1179	
	T3S4A	0.0507	0.961		0.468		0.5101	
	T3S5A	0.0941	2.3541		0.3187		0.4761	
	T3S6A	0.1377	1.9808		2.4745			
	T3S7A	1.066	2.6781		5.3453		0.1897	
	T3S8A	0.0625	7.7695		18.8519		0.3694	
	T3S9A	0.3596	16.0469		63.1953			
	AZ311A	0.0607	6.0491		4.8374		1.3306	
	AZ312A	0.0578	6.2226		5.3102		0.0342	
	AZ313A	0.057	6.2967		5.4197		0.0313	