

Determining the concentration of calcium, potassium, magnesium, and zinc cations leached from solid waste generated by the Norske Skog Tasman Pulp and Paper Mill under varying pH conditions.



Image taken and provided by Dan Hikuroa

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Abstract

As a result of the industry at the Norske-Skog Tasman Pulp and Paper Mill in Kawerau, New Zealand, solid waste is deposited onto a landfill on-site adjacent to the Tarawera River. The solid waste is exposed to the climatic conditions of the region and contaminants may leach from the material into the surrounding environment and river. In this study I examined under what pH conditions calcium, potassium, zinc, and magnesium cations leach from the solid waste. Furthermore, I examined whether the concentration of cations leached from the waste material increased if the amount of sample used was also increased, and the concentrations of cations leached from the sample over time. Adapting the US EPA's TCLP method to what was practical given the time and material constraints I faced at the University of Auckland I was able to examine these questions. Using atomic absorption spectrophotometry I was able to determine the cation concentrations in the extracted liquid. My results indicate potassium, calcium, and magnesium concentrations in the extraction liquid were greater under more acidic conditions. This study cannot conclude whether zinc exhibits similar behavior; zinc was found in low concentrations in the de-ionized water in comparable concentrations to the samples prepared with solid waste material. For the second part of my study I found that if the amount of solid sample I used was greater while using the same amount of extraction liquid the concentration of the cations in the extracted liquid increased. Finally, over time cation concentration as a whole increased. The rate of change decreased over time, and in some cases the cation concentration in the extracted liquid appeared to level off after a week of exposure to the extraction liquid. These studies suggest that a significant concentration of calcium, potassium, and magnesium cations is leaching from this solid waste material into the environment surrounding this landfill site.

Introduction

Leachate tests are a standard procedure in determining whether contaminants are leaching from solid or liquid waste into their surrounding environment. As such these tests have importance in determining the safety of landfills and other disposal methods—particularly whether contaminants are leaching from the waste into groundwater. Groundwater contamination is a global safety concern and to test whether contaminants are in fact leaching from wastes the United States' EPA has developed a test, known as a Toxicity Characteristic Leaching Procedure (TCLP), to examine what compounds are leaching from the waste under varying conditions.¹ Furthermore, there are many standard sets of conditions and limits that have been developed in order to evaluate if a contaminant is at a toxic concentration.² After performing a TCLP test the results can then be easily analyzed and compared to existing safety recommendations, and the safety of a particular landfill practice to the surrounding environments can be evaluated.³

In Kawerau, located on the North Island of New Zealand, the Norske Skog Tasman Pulp and Paper Mill utilizes local landfills to dispose of solid waste from industrial processes. Though not classified as toxic, this solid waste will likely contain numerous contaminants resulting from the pulp and paper processes used at the mill.⁴ This waste is then dumped at a site exposed to the elements, proximal to the Tarawera River. During my investigations I analyzed under what pH

¹ US EPA.

² Davis.

³ US EPA.

⁴ Norske Skog; SKM.

conditions calcium, magnesium, potassium, and zinc cations leach from this solid waste into the surrounding environment using a variant of the TCLP procedure. Additionally, I looked at the concentrations of cations leaching from the material over time to examine the longer term impact on the surrounding environment. Finally, I varied the amount of solid that I used in order to examine the relationship between the amount of solid and the amount of cations that are released.

I hypothesized that the concentrations of these cations that are released will be greater in solutions of lower pH due to the increased dissociation of the solid material under acidic conditions.⁵ Furthermore, exposing an extraction liquid to the solid waste sample for a longer period of time will also result in creating a greater concentration of cations in the extracted sample. The longer a liquid is exposed to the solid the more opportunity for the solid to break apart and come into contact with the liquid and release cations. Finally, adding more solid waste to the mixture will increase the amount of cations present in the filtered extraction liquid. More solid will be in contact with the liquid and greater concentrations of cations will be released. Having obtained data on the cation concentrations found in the adjacent Tarawera River,⁶ I assessed this landfill as a possible contaminant of this local water source.

My experiments aim to investigate under what pH conditions cations leach from solid waste dumped onto landfill sites at the Norske Skog Tasman Pulp and Paper Mill, if the amount of solid waste is related to the concentration of leached cations, and how the cation concentration leaching out varies over time. These studies have significant implications regarding landfill waste practices. Cations are often harmful to the environment and waste must be disposed of in a manner as to not cause any harm. By comparing pH sample data to conditions at the mill and the cation concentrations to US EPA safety guidelines we can examine this landfill site as a potential source of contamination to the surrounding environment including the Tarawera River.

⁵ Zhang.

⁶ Wolfe, Pages 14-18.

Background

Norske Skog has pulp and paper mills throughout the world, including a branch in Kawerau, New Zealand (Figure 1).

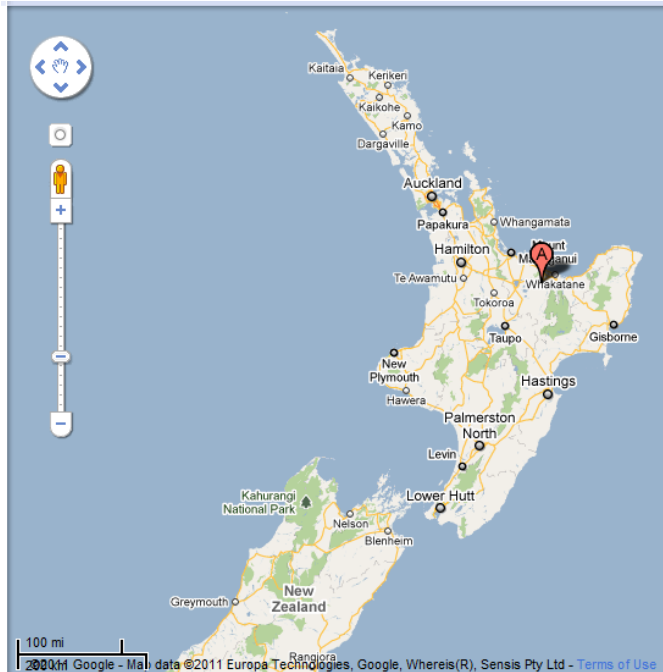


Figure 1. Location of Kawerau and the Norske Skog Tasman Pulp and Paper Mill on the North Island of New Zealand. Image taken from *Google Maps*.

This mill is located south of the Bay of Plenty, adjacent to the Tarawera River. The location in Kawerau is ideal for the mill's purpose—drawing on the region's geothermal resources for energy and situated within the Kaingaroa Forest which the mill utilizes for its' *radiata pines*. The mill utilizes the timber for its products, producing an estimated 300,000 tons of paper per year.⁷ The means necessary for pulp and paper processing create many air, liquid and solid wastes. In 2009, it was reported that the total amount of waste, air emissions, solid and liquid wastes, totaled approximately 582000 tons plus 182000 tons of ash emissions.⁸ Approximately 8% of this waste is reported to have gone into landfills during this year, or 46560 tons (see Figures 2 and 3).⁹

⁷ Wikipedia.

⁸ Norske Skog, Page 106.

⁹ Norske Skog, Page 107.

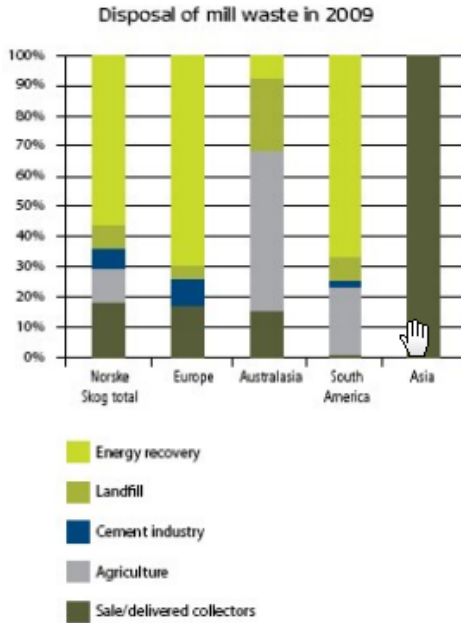


Figure 2. This figure outlines the disposal of waste from the Norske Skog mills. Only a small proportion of mill waste goes into landfills, including the one where the sample I used was taken. *Image taken from Norske-Skog.*

Mill waste is generated at the Norske Skog Pulp and Paper mill through a variety of processes, principally wood debarking, pulp manufacturing, bleaching, paper manufacturing and pulp drying and preparation.¹⁰ During this process a variety of wastes, including metals and other chemicals, are produced. The principle components of solid waste are produced during wastewater treatment and during chemical pulping.¹¹ Some of this solid waste, including paper and unused bark, can be recycled or reused. Other waste, particularly lime sludge and ash, is placed into a landfill.¹² Contents of this waste can include a variety of chemicals, metals and other compounds, including NaOH, HCl, H₂SO₄, Pb, CN, H₂O₂, Cl, PCBs, dioxins, waste sludge, VOCs and phenols.¹³

¹⁰ World Bank Group, Page 396.

¹¹ US EPA.

¹² World Bank Group, Pages 396-397.

¹³ Wolfe, Page 5; SKM.

Total production waste generated by Norske Skog mills 2009

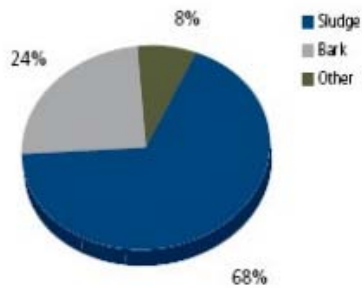


Figure 3. This figure illustrates the composition of waste produced by the Norske Skog mills. Approximately 8% of this material will go into landfills. *Image taken from Norske Skog.*

The landfills utilized by the Norske Skog Pulp and Paper Mill are located near the mill, near Lake Rotooitipaku, and proximal to the Tarawera River (see Figure 4).



Figure 4. A view of the solid waste landfills, located in Kawerau. The river shown is the Tarawera River, just to the right of the landfill sites. *Image taken from Google Maps.*

The site of the landfills is not ideally located for limiting negative impacts on the surrounding environment. The site features relatively shallow groundwater channels and is quite close to the Tarawera River. Furthermore, the Tarawera River is located down from the landfill

site; runoff and groundwater will flow to the river, carrying pollutants with it.¹⁴ Previous studies have tracked contamination of the Tarawera River, particularly its' cation concentrations.

In the environment the solid waste spread over a landfill site is exposed to all weather conditions. Inevitably, water will seep through this solid waste and join the groundwater below. This may feed into the Tarawera River or be transported by other channels. Regardless, this liquid, after leaching through solid waste, may be further contaminated. In my project I examined liquid that over different time intervals, over different amounts of solid waste, and at different pHs leaches through a solid waste sample from the Tasman Pulp and Paper Mill landfill site.

To analyze leachate, or solid waste samples, there are a few common methods. The most utilized and reported is the TCLP method, or Toxicity Characteristic Leaching Procedure, created by the United States' EPA. TCLP testing is used to determine whether solid or liquid waste contains contaminants and ought to be classified as hazardous waste. This determination can then lead into the effectiveness of the disposal system in question.¹⁵ The TCLP test is not designed to estimate the potential or ability of contaminants to leach from the solid waste to a groundwater source.¹⁶ It only examines what contaminants the leachate specifically contains and is depositing into the surrounding environment. These test characteristics are appropriate for analyzing the solid waste at the landfill site.

TCLP tests can be done on both solid and liquid samples. In my case, having obtained solid waste material from the Norske-Skog industrial site, I have adapted the protocols outlined for solid waste samples by the Pollution Prevention Institute.¹⁷ According to the standard procedure, the solid waste sample should be mixed with a suggested acidic extraction liquid, approximately 20 times the weight of the solid waste sample.¹⁸ The extraction fluid must then be mixed with the solid sample for upwards of 18 hours. Following a complete mix the solid must be filtered out, and the remaining liquid simulates what contaminants and compounds would have seeped out of the leachate if the solid waste was in the environment. The EPA TCLP standards recommend a 0.6-0.8um glass fiber filter.¹⁹ This liquid sample can then be analyzed

¹⁴ SKM.

¹⁵ US EPA.

¹⁶ US EPA.

¹⁷ Davis.

¹⁸ Davis.

¹⁹ US EPA.

for its components and any contaminants.²⁰ This procedure provides a thorough analysis of leachate and its protocol can be adapted for my purposes to study the Norske Skog landfill solid waste using the resources available at the University of Auckland.

Hypotheses

The major cations I examined include Ca, Mg, K, and Zn. These metals were chosen due to their identified presence in the Tarawera River in previous studies.²¹

- In the experiments varying pH, the samples mixed in an extraction liquid of lower pH will show a larger concentration of cations in the AAS tests. Increasing the acidity of a solution increases the dissolution capacity of the liquid and consequently the solid waste will be more easily broken apart.²² Consequently more solid waste will be exposed to the liquid increasing the cation concentration in the sampled liquid.
- When observing the cation concentration present in the extraction liquid after varying amounts of time there will be an increased concentration of all cations during the longer time frames. The longer that the solid waste is exposed to the extraction liquid the more opportunity the solid will have to break up and dissolve, adding cation concentration to the liquid. The extraction liquid likely will reach a saturation point in which all of the cations that can leach from the solid will be present in the extracted liquid.
- In the experiment varying the amount of solid exposed to the extraction liquid, the samples with greater amounts of solid will likewise exhibit higher cation concentrations. More solid waste will contain more cations; when exposed to approximately the same amount of extraction liquid and the same mixing conditions the extraction liquid will see an increase of cation concentration.

Materials and Methods

To complete my experiments I altered the TCLP procedure based on what materials were available to me at the University of Auckland (Table 1).²³ I also wished to examine a few

²⁰ Davis.

²¹ Specifically in comparison to data obtained by Angela Slade, *Frontiers Abroad*, and reported in Wolfe, “*Concentrations of Selected Ions in Groundwater at Tasman Pulp and Paper Mill Site.*”

²² Zhang.

²³ All of my procedure was developed with the assistance of Angela Slade.

additional characteristics of this solid waste; specifically, using extraction liquid at different pH conditions, monitoring the pH and cation concentrations over time, and varying the amount of solid and examining the subsequent concentration of cations found in the liquid.

To begin my experiments, I collected solid waste samples with the help of Dan Hikuroa and the *Frontiers Abroad Earth Systems Science Auckland* crew at the Norske Skog Tasman Pulp and Paper Mill landfill site. The sample was collected from the surface of landfill site.

For the first experiment, varying the extraction liquid pH, I mixed approximately 40 mL (~40 grams) of liquid at the appropriate pH level, 2, 3, 4 and 5, with about 2 grams of the solid sample obtained from the landfill site in a 50mL centrifuge tube. This is scaled down from the TCLP recommendations of 100 grams of solid sample mixed with 20X that weight of extraction liquid in order to utilize the centrifuge tubes available yet maintaining the same ratio. The extraction liquids used in the TCLP procedure are variants of HCl and nitric acid. For simplicity in this experiment I used 70% concentrated nitric acid, diluted to the proper pH level. This was accomplished by filling a large 500mL beaker with DI water and then adding nitric acid dropwise until the approximate pH desired was recorded using a pH meter. The solid waste sample was used as it is, not chemically dried. This was in an attempt to simulate conditions as they would be in the environment when the solid waste was dumped at the landfill site and its subsequent interactions within the environment in addition to an attempt to minimize any contamination from other chemicals and vials.

After adding the extraction liquid to the solid sample, I allowed the samples to mix for 4 hours after shaking vigorously for 10 minutes. The pH level was recorded before mixing the extraction liquid and then after the 4 hours had elapsed (see Appendix for initial and final pH data). Then using a 0.45 filter and syringe the liquid was filtered from the solid waste sample, halting the leaching process. This liquid then became my sample, to be analyzed using atomic absorption spectrophotometry (AAS). Samples were refrigerated in the centrifuge tubes until analyzed using the AAS. The liquid was analyzed for Ca, Mg, K, and Zn which were all identified in the Tarawera River. The control for this experiment consisted of only DI water in a centrifuge tube. This liquid was then likewise be analyzed for cations to examine any potential influence from the tube itself. The samples from this portion of my experiment were done in triplicate to reduce any errors or variation. All graphed values in the analysis portion of this report were compiled with the average of the three samples.

For the second part of my experiment, in which I adjusted the time that solid samples are allowed to mix with extraction liquid, I used samples at pH 2, 3 and 5. These samples were allowed to mix at different time intervals: 1 hour, 2 hours, 4 hours, 7 days, and 28 days to determine if the cation concentration leached varies with time. In order to run the analysis on the extraction liquid I prepared the samples as in the varying pH experiments, with approximately 2 grams of solid sample mixed with 40mL of the extraction liquid.

Finally, I varied the amount of solid waste I used, from 2 grams to 4 grams and 8 grams. Evaluating these amounts at two different pH levels, 3 and 5, I was then able to see if the concentration of cations in the extracted liquid is related to the amount of solid waste. The samples were prepared as in the previous experiments except with the changes in the amount solid waste and extraction liquid to keep total weight the same.

In these experiments I measured the pH of the DI water used in each sample, the pH of the extraction liquid prior to adding leachate and the pH after extraction. This liquid was analyzed for its cation concentrations using the AAS. In order to complete this analysis various standards had to be used, three for each element analyzed. These standards, for Ca, Mg and K, were prepared using 1000 μ g/mL standard solutions and then diluting them (dilutions are listed in the Appendix). For example, in analyzing calcium I used dilutions of 63.4ppm, 31.7ppm and 15.85ppm to create a standard curve. To create the standard curve for zinc I used dilutions prepared by other individuals in the School of Environment at the University of Auckland. These dilutions were used after estimating parts per million range using the AAS and then creating a linear or least squares regression plot of standards covering the sample point. This project was completed between 20/3/2011 and 13/5/2011.

Table 1. Materials List.

Materials:
<ul style="list-style-type: none"> • 50 mL centrifuge tubes (approximately 100) • 0.45 filters (between 26 and 100) • Syringes (to be used with filters) • Filter paper (maybe) • DI water • Nitric Acid (70%, concentrated) • Balance • pH meter • Stock solutions, 1000µg/mL of Ca, K and Mg • Pre-prepared Zn dilutions

Complied with the assistance and guidance of Angela Slade and Russell Clarke.

Results

The first experiment I completed was the analysis of the liquid leached through the solid waste with varying initial pH. Once the samples had sat for four hours the liquid was filtered out and placed in a clean centrifuge tube to be analyzed via AAS. Results of this analysis are listed in Table 2 and graphed in Figure 5.

Table 2. Varying pH Experiment Results: Cation Concentrations. Listed below are concentrations of cations Calcium, Magnesium, Potassium, and Zinc as recorded by the AAS. Concentrations are listed in µg/mL or ppm.

Sample ID	[Ca] µg/mL	[Mg] µg/mL	[K] µg/mL	[Zn] µg/mL
CH01 (DI)	ND*	ND	7.016	0.049
CH02 (pH =2.28)	High*	4.237	4.509	0.021
CH03	High	-0.263	4.705	0.043
CH04	High	6.216	3.354	-
CH06 (pH=3.27)	17.352	3.266	3.512	0.016
CH07	12.329	2.781	3.388	0.021
CH08	9.027	1.399	3.023	0.010
CH15 (pH=4.19)	-0.227	1.090	2.849	0.003
CH16	1.178	1.808	3.043	0.009
CH17	0.320	1.441	3.134	0.014
CH12 (pH=5.13)	-1.001	1.860	2.742	0.003
CH13	0.770	2.525	3.196	0.006
CH14	0.133	1.630	2.957	0.006

*Notes: 1) ND stands for “None Detected.”

2) HIGH reveals very high concentrations that could not be determined accurately using the available standards.

3) Entries replaced with a – indicate that after performing Ca, K, and Mg analyses not enough sample remained to complete the indicated analysis.

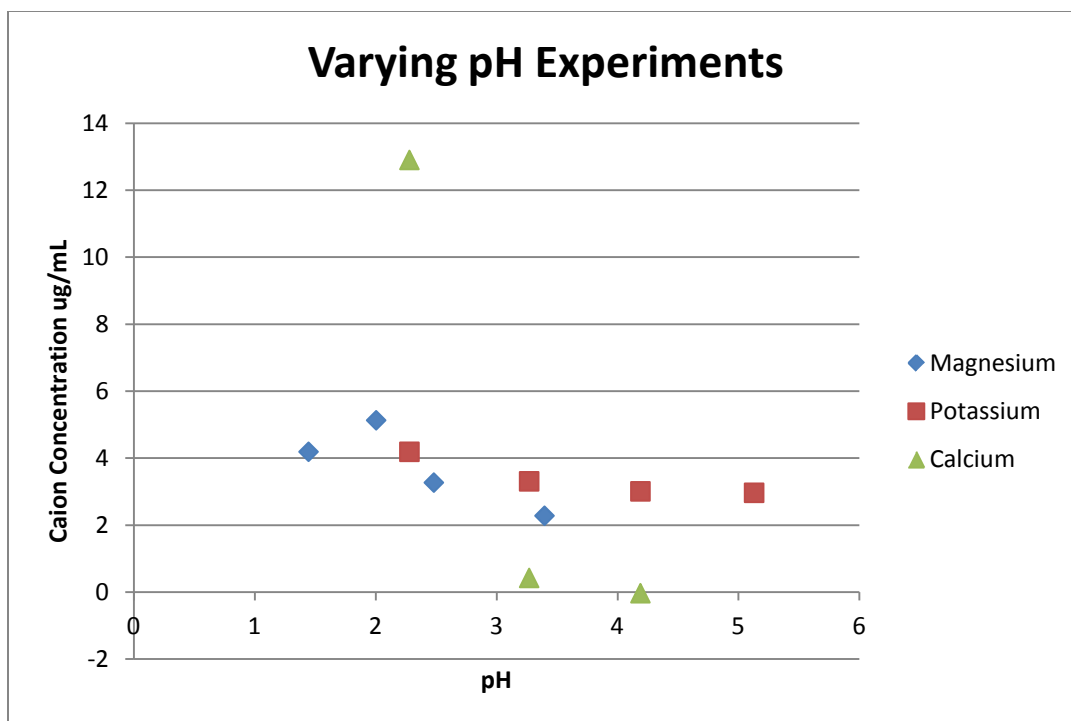


Figure 5. Graphed results of the experiments in which pH was varied. Cation concentration in the extracted liquid was measured after 4 hours. The amount of solid waste sample used was held constant, approximately 2 grams, through all trials. This graph indicates that as pH level increased, the cation concentration found in the extracted liquid decreased.

Notes: 1) All points were plotted by finding the average of the three samples at a given pH.

2) There are only three points for calcium used. For pH 2.28 concentrations of calcium were too high to be accurately detected by the AAS. As such this indicates they are higher than any points on this graph and support my hypothesis.

3) Zinc was not included as its concentration in the extracted liquids did not vary significantly from sample to sample. Additionally because of the presence of zinc in the DI water alone it is undetermined if the zinc present in the samples is from the solid waste sample or the DI water.

Preliminarily these results reveal that greater concentrations of calcium were leached from the solid waste under the most acidic conditions, at a pH of 2.19 and then 3.27. Results for calcium concentration were comparable at pH levels 4.19 and 5.13. Likewise, the highest concentrations for magnesium cations were found at pH levels 2.19 and 3.27. Concentrations of magnesium at pH 4.19 and 5.13 were lower and comparable to each other. Potassium concentration was also highest at pH 2.28. Results for concentration at pH 3.27, 4.19 and 5.13 are also comparably lower. Zinc concentrations did not follow these trends; concentrations of zinc in the extracted liquid were lowest at pH 5.13. It should be noted that in the sample of only DI water a higher concentration of zinc was present than in many of the samples with solid waste material. This suggests that there is underlying zinc in the water used in these experiments and the sample results are consequently unreliable. It cannot be determined through these experiments whether

zinc concentration is due to the solid waste or to the DI water used. Additionally, all recorded concentrations of zinc are very low with few significant differences between samples.

In the next set of experiments solid waste material was allowed to mix with the extraction liquid for a varying amount of time, from 1 hour to 4 weeks. The results from this set of experiments are listed in Table 3.

Table 3. pH Level Over Time Experiments: Cation Concentrations.

Sample ID	[Ca] µg/mL	[Mg] µg/mL	[K] µg/mL	[Zn] µg/mL
CH05c (pH=2.62)	48.897	5.389	5.343	0.034
CH05a	53.647	5.447	8.315	-
CH05b	56.414	9.639	7.845	0.024
CH19 (pH=2.59)	41.760	6.142	4.201	0.017
CH09 (pH=2.61)	50.570	9.631	5.323	0.008
CH21a (pH=3.70)	-0.063	-0.044	1.969	0.009
CH21b	0.994	1.061	2.816	0.010
CH21c	3.718	3.751	4.414	0.012
CH18 (pH=3.80)	2.963	2.040	3.501	0.009
CH10 (pH=3.54)	24.513	7.546	4.365	0.004
CH22a (pH=5.45)	ND	ND	1.893	0.013
CH22b	ND	-0.068	2.470	0.010
CH22c	-0.131	2.035	4.404	0.007
CH20 (pH=5.26)	11.812	6.734	4.783	0.003
CH11 (pH=5.66)	25.367	8.283	4.494	0.004

Notes: 1) Blue text indicates one set of data at one pH level, ~2.62; 1 hr, 2 hrs, 4 hrs, 1 week and 4 weeks. Green and black indicate other sets of data at different pH levels, ~3.7 and ~5.5 respectively.

2) Entries replaced with a – indicate that after performing Ca, K, and Mg analyses not enough sample remained to complete the indicated analysis.

Overall data indicates that the cation concentration leached from the solid waste sample increased over time. There are several exceptions within the data but are easily accounted for by the fact that each solid sample may have different greatly in compactness, source, and content. Looking at the data set with pH=2.6 the calcium, magnesium, and potassium concentrations leached did not vary as much as the others; cation levels remained approximately constant suggesting that at a very low pH the same concentration of cations are released, perhaps explained that under a low pH more cations are released in the same amount of time. Dissociation occurs more quickly under acidic conditions so concentration will not vary over longer periods of time. This is observed for cations magnesium and potassium as well. Other results for calcium, potassium, and magnesium under the other pH conditions show an increase in cation concentration over time. When examining zinc concentrations in the extracted liquid I again found extremely low concentrations that varied little from sample to sample. In what small

variation I observed, cation concentration seemed to increase over a short period of time, between 1 and 2 hours, but then show no significant correlation.

Next I examined whether varying the amount of solid waste sample exposed to a volume of extraction liquid led to any change in cation concentrations found in the extraction liquid after four hours. Results are listed in Table 4 and graphed in Figures 6 and 7.

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

Sample ID	[Ca] $\mu\text{g/mL}$	[Mg] $\mu\text{g/mL}$	[K] $\mu\text{g/mL}$	[Zn] $\mu\text{g/mL}$
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.

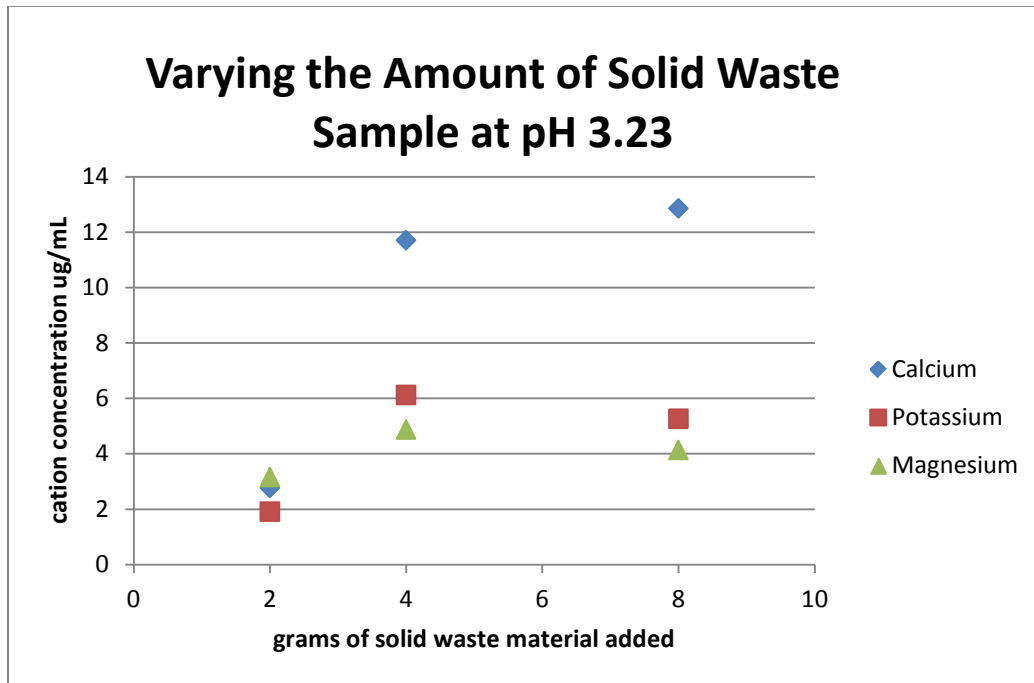


Figure 6. This graph shows the cation concentration observed in the sample vials prepared using different amounts of solid waste material at pH 3.23. All samples were allowed to mix with the extraction liquid for four hours. On this figure it can be observed that from 2 grams of sample to 4 grams the cation concentration found in the extracted liquid increased. From 4 grams to 8 grams for potassium and magnesium the concentration decreased slightly. Calcium concentrations did not show this decrease, continuing to increase with the addition of more solid waste material.

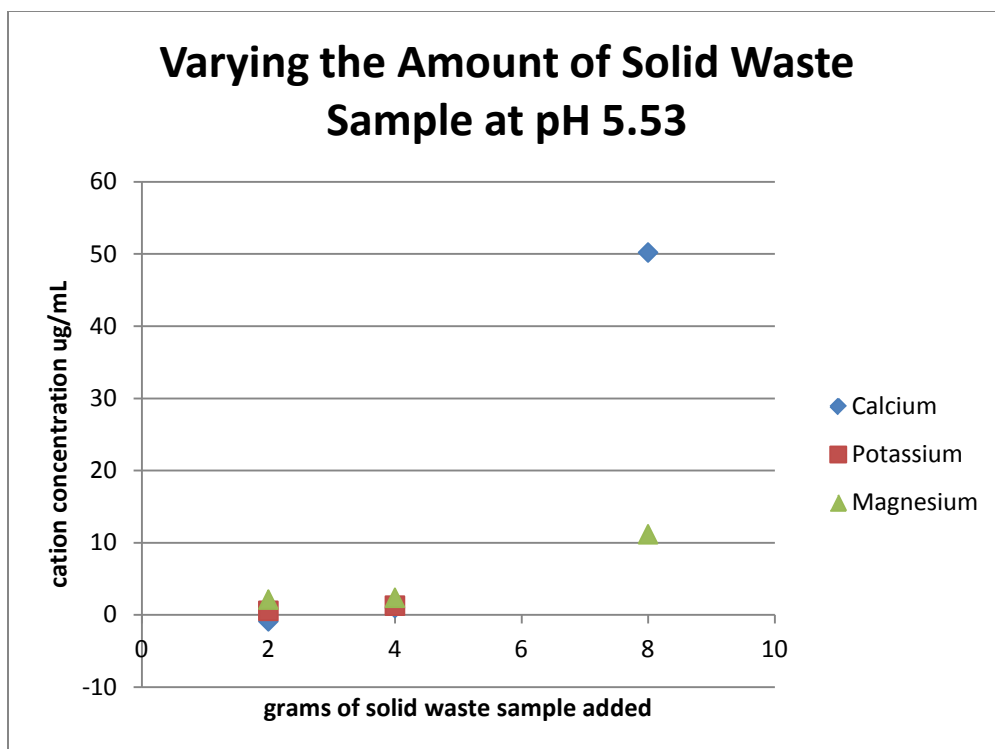


Figure 7. This graph shows the cation concentration observed in the sample vials prepared using different amounts of solid waste material at pH 5.53. All samples were allowed to mix with the extraction liquid for four hours. From this figure it can be seen that cation concentration in the extracted liquid increased with an increase in the amount of solid waste sample added. Again zinc concentrations are not shown.

Note: There are only two data points listed for potassium. This is due to the fact that the third, using 8 grams of solid waste material, had a higher cation concentration the AAS could accurately read. This supports the trend shown by the other data.

In this set of experiments, my results suggest that as the amount of solid sample increases the concentration of cations found in the extracted liquid also increases. In several cases, including calcium, magnesium, and potassium, the concentration of cations in the extracted liquid increased as the amount of solid sample increased from 2 grams to 4 grams, but then remained approximately constant from 4 grams to 8 grams. Zinc remained relatively constant at very low concentrations in all of my samples. Looking at calcium, magnesium and potassium concentrations though suggests the possibility of a saturation point. Further experimentation is necessary to explore whether these are just particular samples, as in magnesium samples CH23, 25 and 27 or are the exception, compared to magnesium samples CH24, 26 and 28. Additionally, it should be noted that again the samples at a lower pH, 3.23 verses 5.53, showed greater concentrations of cations in the extracted liquid in many samples.

Discussion

My results suggest that calcium, magnesium and potassium cations are leaching from the solid waste material generated from the pulp and papermaking processes at the Norske Skog Tasman Pulp and Paper Mill. The solid waste, once deposited on the landfill site, is exposed to climate and rainwater conditions. My experiments demonstrate that these cations are leaching from the solid waste material to the surrounding environment.

In my experiments varying the pH of the liquid I found that under more acidic conditions more cations leached from the solid material. This is likely due to the dissociative nature of acids; it is consequently more successful at breaking up the solid waste material. This is a concern when examining the climate conditions in Kawerau, New Zealand. Rainwater typically has a pH of around 5.5-6.5. Though a pH of 7 is neutral, rainwater is often slightly more acidic due to its exposure to carbon dioxide in the atmosphere. Carbonic acid is the result and the pH of rain is lower than neutral. Rain is classified as “acid rain” when its’ pH is below 5.6. Currently New Zealand does not face problems with acid rain due to the warm climate and the relatively low air pollution levels. This suggests that rain water coming into contact with the solid waste on the Kawerau landfill site is at a pH ranging from 5-6. This is a level in which my results suggest cation concentration in the extracted liquid exists but is not at its highest levels. Nonetheless calcium, magnesium, and potassium cations will be leached from the solid waste into the environment under these conditions.

Varying the time that the solid waste sample was exposed to the extraction liquid suggests that over a longer period of time more cations will be released from the waste; cation contamination will continue considerably longer than after initial exposure to the environment. My data suggests that for up to a week of intense exposure to the extraction liquid cation concentration in the extracted liquid continues to increase. It should be noted that this excludes the amount of time that the solid waste sample had already been exposed to the environment on the landfill site prior to sampling. As such, it cannot be determined from these experiments what the total time frame for the rate of contamination to decrease is. My results do demonstrate however that the rate of change of contamination does decrease over time and may drop off significantly after at least a week of exposure to the extraction liquid. This is consistent with my hypothesis; over time more of the solid waste will be exposed to the extraction liquid allowing cations to leach from the solid material. However, after a significant amount of time has passed

many of the cations from the solid waste will have already leached into the surrounding environment explaining the decrease in emitted cation concentration over time. This consequently means that even after dumping on the site, landfill waste will continue to pollute the surrounding after for a significant amount of time.

Finally in the course of my experiments I examined the relationship between the amount of solid waste exposed to an extraction liquid and the cation concentrations found in the filtered liquid. As the amount of solid waste increased the cation concentration likewise increased. Again, more of the solid will be exposed to the extraction liquid and consequently more cations can be released. My results may suggest that up to a certain amount of solid waste the amount of cations it emits will likewise increase. My data does show that from 4 grams to 8 grams there was not always an increase in cation concentration emitted, suggesting a maximum capacity to the extraction liquid. This is likely to be even more distinct in the environment; the solid waste is layered thickly and often compacted together. This may inhibit cations from being leached into the surrounding environment. However, as the landfill site is exposed to rain and actual climate conditions likely a saturation point won't exist—new liquid will constantly be streaming through the solid waste material.

It should be noted in all of these experiments that the solid waste varied greatly from sample to sample. Some of the solid waste was very hard, stuck in clumps, while other pieces broke apart easily when exposed to the extraction liquid. There is no way to account for these differences except via chemical drying which in the case of this experiment was not done. By not drying the solid waste my experiments more accurately simulate the actual conditions on the landfill site.

In order to fully determine whether cations leach out from the solid waste deposited on landfills at the Tasman Pulp and Paper mill under more acidic conditions, further experimentation is necessary. I recommend repeating experiments at set pH levels, at approximately 1, 2, 3, 4, 5 and compared against DI water. Given the tools available at the University of Auckland I was unable to examine pH levels much below 2. Furthermore, by titrating extraction liquids, more precise increments can be reached. Additionally, further studies can be completed regarding amount of solid waste and the time exposed to an extraction liquid.

I also recommend completing further studies examining both what is leaching from the solid waste, including but also expanding from the four cations I examined, and where

contaminants are traveling. The Tarawera River is quite contaminated and features concentrations of all the cations I observed leaching from my solid samples; it ought to be investigated whether these contaminants are coming from this landfill site or from another point along the river's course. Regardless, contamination should be tracked from the landfill; whether it is traveling into the ground, the Tarawera River, other groundwater sources, or elsewhere.

Research into the safety of this landfill site and others around New Zealand is of paramount importance in minimizing environmental contamination. From my studies I have found that significant concentrations of calcium, magnesium, and potassium are leaching from the solid waste deposited at the Tasman Pulp and Paper Mill landfill. Given the topography of the site and the adjacent Tarawera River it is likely that contaminants from the landfill site are affecting the concentrations found in the river. My experiments have not been able to identify whether zinc contamination is also created by the landfill site. All of the zinc data I obtained is in incredibly low concentrations and comparable from sample to sample. Further experimentation is needed to examine potential zinc contamination.

Conclusions

In this study I developed a procedure based off of US EPA TCLP testing to examine the cations leached from the solid waste deposited onto a landfill site at the Tasman Pulp and Paper Mill. Using extraction liquids of varying pH I was able to examine under what conditions increased concentrations of cations leached from the solid waste. Additionally I examined the effect of cation concentration in the leached extraction liquid through varied amounts of the solid sample as well as over longer periods of time.

My results suggest that decreasing the acidity of the extraction liquid leached through the solid waste sample leads to an increased concentration of the cations Ca, Mg and K in the extracted liquid. Furthermore, using more of the solid sample leads to an increased concentration of cations in the extracted liquid. Finally, my results suggest that over time the cation concentration leached into the liquid increases, though finitely. In my experiments, after a week of exposure concentrations of these cations in the extracted liquid didn't change considerably.

In the case of examining zinc concentrations in the extracted liquids I did not see any correlation as in the cases of Ca, Mg and K. Additionally in the sample of only DI water there was a recorded zinc concentration higher than many of my other samples. This suggests a

background presence of zinc that is consistent with other studies completed in New Zealand that is confounding my results.

These results suggest significant implications for the actual landfill site at the Tasman Pulp and Paper Mill. First that it is clear that metal cations are leaching into the surrounding environment and due to the land gradient quite likely the Tarawera River. In all of the samples I examined the extraction liquid showed concentrations of these four cations. Additionally, adding more of the solid waste material led to an increased cation concentration in the extracted liquid. The landfill site will feature much higher amounts of the solid waste material. This suggests that even higher concentrations of cations will be leaching from the solid waste material on the site into the surrounding environment. Finally, cations continue leaching from the material after deposition. The solid sample I obtained from the site was dry and likely exposed to the environment for a considerable amount of time. Extracting liquid after varying time intervals indicated that the rate of cation concentration leached did decrease over time, but some cations were still emitted.

In order to more fully understand these results and consider the landfill site as a source of contamination of the Tarawera River further experimentation is required. Details on the time frame that waste sits on the landfill site is also required in order to evaluate over what time frame cation leaching into the environment continues. Also data on the pH of rain and groundwater details in Kawerau would be useful in examining the actual conditions the solid waste is exposed to on the landfill site and thus the risk of contamination the site poses.

Appendix

Appendix Table 1. Varying pH Experiments. Listed below are the initial and final pH values measured after the elapsed four hours. Each sample was prepared using approximately 2 grams of the solid waste material. The experiments ranged from an initial pH of values approximately 2, 3, 4 and 5. A control was set up using only DI water and is listed as CH01.

Sample ID	Initial pH (extraction liquid)	Final pH (extraction liquid + solid)	Time elapsed (hours)
CH01	6.35	6.47	-
CH02	2.28	6.33	4
CH03	2.28	6.68	4
CH04	2.28	6.60	4
CH06	3.27	7.59	4
CH07	3.27	7.57	4
CH08	3.27	7.55	4
CH15	4.19	8.65	4
CH16	4.19	8.55	4
CH17	4.19	8.66	4
CH12	5.13	8.15	4
CH13	5.13	8.24	4
CH14	5.13	8.42	4

Appendix Table 2. pH Level Over Time Experiments. Listed in this table are the initial and final pH values measured after a varying amount of time; 1 hour, 2 hours, 4 hours, 7 days and 28 days. Each sample was prepared using approximately 2 grams of the solid waste material. For the varying time experiments, initial pH level ranged from approximately 2.5, 3.5 and 5.5. The control to be utilized here is again sample CH01 of only DI water, left in the 50mL centrifuge tube.

Sample ID	Initial pH (extraction liquid)	Finals pH (extraction liquid + solid)	Time elapsed
CH05c	2.62	7.19	1 hour
CH05a	2.62	7.44	2 hours
CH05b	2.62	7.38	4 hours
CH19	2.59	7.26	7 days
CH09	2.61	7.55	28 days
CH21a	3.70	8.47	1 hour
CH21b	3.70	8.57	2 hours
CH21c	3.70	7.69	4 hours
CH18	3.80	7.75	7 days
CH10	3.54	7.47	28 days
CH22a	5.45	8.94	1 hour
CH22b	5.45	8.89	2 hours
CH22c	5.45	8.50	4 hours
CH20	5.26	7.85	7 days
CH11	5.66	7.12	28 days

Appendix Table 3. Varying Amount of Solid Experiments. Listed below is the varying amount of solid used in each of these samples and the recorded initial and final pH level of the samples after four hours elapsed. Two different pH levels were used, about 3.5 and 5.5

Sample ID	Amount of Solid (g)	Initial pH	Final pH	Elapsed Time
CH23	2.0169	3.23	7.18	4 hours
CH25	4.0493	3.23	7.75	4 hours
CH27	8.0131	3.23	7.37	4 hours
CH24	2.0579	5.53	8.38	4 hours
CH26	4.0072	5.53	7.92	4 hours
CH28	8.0194	5.53	7.48	4 hours

Appendix Table 4. In order to use the AAS I had to create three standard solutions for each cation I analyzed. Reported below are the concentrations used to create the standard curves.

Cation	Dilutions ($\mu\text{g/mL}$)
Ca	63.4
	31.7
	15.85
Mg	10.84
	5.42
	2.71
K	10.84
	5.42
	2.71
Zn	50.405*
	20.044*
	10.080

* Indicates that the dilutions used for that sample were prepared by another member of the School of Environment at the University of Auckland. All other dilutions I prepared using provided stock solutions.

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