

# Concentrations of Selected Ions in Groundwater at Tasman Pulp and Paper Waste Site

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## Abstract

Pulp and paper mills generate a significant amount of contaminated waste material, much of which is dumped into landfill areas. One notable waste site exists at Lake Rotooitipaku in Kawerau, New Zealand, where the Tasman Pulp and Paper Mill has been dumping solid waste since the 1960's. Due to the toxic nature of this site, many concerns have been raised over the impacts it may have on the surrounding area. In an attempt to better understand the hydrology of the area, the chemicals that have been deposited there, and the long-term effects that the landfill may have, this study analyzes selected ions in groundwater around the waste site. Comparing this data to previous site assessments, our analysis shows that there is significant variation in ion concentrations across the waste site, as well as with depth. Current data also shows that concentrations of some ions have changed considerably since the last site assessments conducted in 2006. Given the complex nature of the waste site, this study argues that more consistent testing is needed at the landfill in order to accurately monitor the movement of potentially harmful contaminants. This type of groundwater assessment is crucial to the development of protection strategies and water resource planning in the Kawerau area.

## 1 Introduction

Until the early 1960s, Lake Rotooitipaku was a shallow body of water, rich in ecological diversity and active hot springs (Tull, 2007). While this lake and the surrounding area have important cultural and spiritual significance for the Maori people, local iwi tribes were forced to lease the land to the Norske Skog Tasman pulp and paper mill in 1964 when the company was given legal permission to create a waste disposal site there. Since then, the lake has been inundated by solid waste. As a result, the lake no longer acts as a waterway for migratory fish and eels, the geothermal surface features and hot springs in the area have been ruined, ponds that have formed behind large constructed embankments are suffering ecologically, and contamination has migrated offsite (Tull 2007). The degradation of this space is especially concerning due to the fact that the lease agreement expires in 2013, at which point the land and liability of the site will be transferred back to the local Maori trust. Due to their concerns regarding the contamination of the site and its larger impact on ecological and human health, the Maori trustees and local residents in Kawerau have expressed the urgent need for site remediation, ongoing environmental monitoring, and evaluation. Comparing past site assessments with current data, this study analyzes selected ions in groundwater at the Rotooitipaku waste site in order to show how they vary seasonally, spatially and with depth. This type of groundwater assessment is a necessary aspect of development strategies that work to protect the surrounding area from contamination and for water resource planning in the Kawerau area.

## 2 Background

### 2.1 Site Description

The Tasman Pulp and Paper mill is located about 300 meters to the east of the Tarawera River in Kawerau, Bay of Plenty, New Zealand (Figure 1). The mill was established in 1954 to increase industry in the Bay of Plenty and to process timber from maturing forests of radiata pine (*Pinus radiata*) in the state-owned Kaingaroa Forest (Te Ara Encyclopedia). Since then, the mill has grown to produce over 350,000 tons of newsprint and 200,000 tons of kraft market pulp each year, supplying all of New Zealand's newsprint and about 30% of Australia's (Norske Skog). The plant has become one of the largest consumers of energy in the country and has recently developed its own geothermal wells to power its year-round production (Frye, unpublished).



**Figure 1. Location of Norske Skog Pulp and Paper Mill in Kawerau, New Zealand (Labeled as A). Image obtained from Google Maps.**

The mill was originally built in Kawerau because of its close proximity to geothermal energy, as well as the Tarawera River. For years the river was used to dump the mill's pulp and paper waste. However, in 1964 the Tasman Pulp and Paper Enabling Act gave the Tasman company permission to create a waste disposal site on Maori Trust land at Lake Rotootipaku (Tull 2007). This site is located several kilometers northwest of the mill in Kawerau and approximately 3 kilometers west of the Tarawera River. Originally a scenic lake surrounded by sacred Maori land, the site soon became the Tasman mill's primary solid waste disposal area. Since then, sludge waste from the mill has inundated Lake Rotootipaku, covering it with more than 20 meters of material. The extent of this coverage can be seen in Figure 2, where the waste material is distinguishable by its tan color. From 1971 to 1995, this waste was dumped untreated, despite it containing significant amounts of hazardous contaminants such as zinc hydrosulphite



### *Pulping*

Pulping is the initial stage of papermaking and provides the processed material. Pulp making begins with preparation of the wood. Typically, a mill will have an on site log pile that the raw materials are taken from. These logs are debarked and chipped, with the waste bark being burned for energy (SAIC).

After preparation, the wood material is broken down into fibers to produce pulp. While there are many methods of pulping, the Norske Skog Tasman Pulp and Paper Mill uses both kraft and thermomechanical processes. The kraft process is a form of chemical pulping which uses a sodium-based alkaline solution (white liquor), consisting of sodium sulfide ( $\text{Na}_2\text{S}$ ) and sodium hydroxide ( $\text{NaOH}$ ), to digest the wood chips (SAIC). Thermomechanical pulping (TMP) involves partially softening the wood with chemicals before pulping with mechanical force under heat and pressure. This type of pulping produces high yields, but the pulp is of low strength and quality. Such pulps are used principally for newsprint and other non-permanent paper goods (SAIC).

### *Pulp Processing and Bleaching*

After pulp production, raw pulps must be processed to remove impurities. The pulp is first washed, screened and defibered to create a more homogeneous mixture (SAIC). It is then chemically treated to recover residual white liquor for reuse. Heavy metals and waste products, such as excess sodium hydroxide ( $\text{NaOH}$ ) and sodium sulfite, are also removed during processing.

Paper pulp is often bleached during processing in order to increase its brightness. Chemical pulp bleaching has undergone significant process changes since the 1990's (pulppasn). At that time, the bleaching process involved the use of elemental chlorine ( $\text{Cl}_2$ ). However, because of environmental and health concerns about dioxins (which are a byproduct of elemental chlorine), pulp mills now use elemental chlorine free (ECF) and total chlorine free (TCF) bleaching technologies.

In bleaching, the processed and refined pulp is chemically altered to increase its brightness. During this process, pulp passes through three to five stages of chemical bleaching and water washing. Besides chlorine, hydrogen peroxide and sodium hydrosulfate ( $\text{Na}_2\text{SO}_3$ ) can also be used in the bleaching process.

### *Paper Manufacture*

Papermaking consists of two primary processes: wet end operations and dry end operations (SAIC). In wet end operations, the cleaned and bleached pulp is formed into wet paper sheets. In dry end operations, those wet sheets are dried to form paper. Various surface treatments are often applied to the paper before the process is complete.

Wet end operations begin with spreading wet pulp onto a moving screen, which is then sent through a series of vacuums and rollers to remove water and press the paper into firmer sheets (EPA). The pressed product is then sent to dry end operations (EPA). The only true waste stream produced during wet end operations is the wastewater that is collected from the pulp. This wastewater contains the same contaminants as that produced during the pulping process, although in much smaller concentrations.

In dry end operations, the paper is driven through steam-heated rollers to further press the sheets and bind the paper fibers together (EPA). The sheets are then sent through machines, which apply various coatings to the paper depending on the desired end product (SAIC). Additives applied to paper products include resins and waxes, fillers, silica, talc,



dyes, and certain inorganic chemicals (calcium sulfate, zinc sulfide, and titanium dioxide) for improved texture, print quality, opacity, and brightness (EPA). After dry end operations are completed, the remaining process water is filtered to remove solids before being recycled. The filtered solids produce a “sludge” that has high concentrations of dioxins and chlorinated substances. This waste poses a large compliance burden for paper mills. While waste is now treated before being disposed of, many older plants dumped this untreated, hazardous waste into landfills, such as the site at Lake Rotooitipaku.

### 2.3 Pollution Outputs in the Production Line

Wood pulping and the production of paper products can generate considerable amounts of pollutants that are all discharged into waste material. From suspended solids to carcinogens such as dioxins, this contamination spans the full spectrum of toxicity and can pose significant threats to human and environmental health. Overall, most of the contaminants associated with pulp and paper mills are introduced at the pulping and bleaching stages, where the majority of chemical inputs occur. Table 1 below lists the common contaminants associated with each stage of paper manufacturing.

| <b>Pulping</b>            | <b>Bleaching</b>          | <b>Paper Manufacture</b>   |
|---------------------------|---------------------------|--|
| Sodium Hydroxide Residues | Hydrogen Peroxide         | Waste sludge   |
| Sulfuric/Sulfurous Acid   | Elemental Chlorine        | Bleaching and Pulp contaminants  |
| Hydrochloric Acid         | Chlorinated Compounds     | SCOVs  |
| Hydrogen Sulfide          | Sodium Hydrosulfite       | VOCs   |
| Ammonia                   | Polychlorinated Biphenyls | Slimicides   |
| Lead                      | (PCBs)                    | Chlorinated Phenols  |
| Cyanide                   | Dioxins and Furans        | Aminos and Quaternary  |
| Zinc                      |                           | Ammonium Compounds   |
| Chromium                  |                           | Silver Compounds   |
| Resin                     |                           | Titanium Residues  |
| Unnatural Fatty Acids and |                           | Oil and Grease Discharges  |
| Chlorinated Analogs       |                           | Polychlorinated Biphenyls,<br>pesticides, dyes, asbestos,<br>fibers from agricultural residues |

**Table 1. Common contaminants associated with each stage of the paper manufacturing process. Table modified from Tull, 2007 and EPA.**

The pollutants outlined above include both organic and inorganic contaminants, as well as a considerable list of heavy metals. The organic contaminants include chlorinated compounds, resins, and fatty acids. The presence of these compounds is important because they form soluble or insoluble complexes with toxic heavy metals, which determines whether the metals will migrate or be retained in the soil. A variety of heavy metals are associated with pulp and paper manufacture, including concentrations of calcium, magnesium, sulfate, chloride, sodium, nitrate, potassium, lignin, and phenol. These metals are present largely due to their use as complexing agents to remove other transition metals found within wood in the pulping process. Many inorganic constituents are also involved with paper processing. These constituents include mercury, manganese, boron, arsenic, phosphorus, and sulfide.

### 2.4 Contaminants in the Waste Site

To try to mitigate flow of contaminants and enclose the disposal area at Lake Rotooitipaku, two embankments have been constructed on the eastern and western sides of the waste site (see Figure 2). The western embankment is approximately 20 meters high and follows the Western boundary of the disposal area. It was constructed using pumice and general mill wastes, including up to ten tons of zinc hydrosulfite. Its primary purpose is to prevent encroachment of waste into A8 pond. The eastern embankment is located on the eastern boundary of the site and runs north to south along the entire waste disposal area. It is similar to the Western embankment in composition and was built to prevent primary waste from migrating into the Tarawera River. Although it is the only structure separating the waste site from the river, it is also used as a service road. This function has potential implications of weakening its integrity and may have been the cause of previous breaches in the 1980's, when the embankment failed three times and sent solid waste into the Tarawera River.

Due to concerns regarding the Lake Rotooitipaku landfill area, a number of environmental site assessments have been conducted over the past 10 years by Sinclair Knight Merz (SKM), Gwilym Environmental Services (GES), and Gulf Resource Management (GRM). These site assessments collectively confirm contamination in the soil and water of the landfill, reporting levels that exceed Australia and New Zealand Conservation Council (ANZECC) guidelines for drinking water, agricultural use, and ecological health and protection.

Groundwater at the site has been tested for a range of parameters including nutrients, heavy metals (e.g. arsenic, mercury, boron, and zinc), and organics (e.g. PCP and dioxins). The groundwater concentrations of contaminants in this site are, in some cases, of magnitudes higher than the guideline levels. Some of the contaminants that exceed guideline values include sodium, sulfate, manganese, copper, lead, and zinc. High levels of these contaminants indicate that groundwater quality at the site is very poor. High contaminant concentrations are also found in the soils and surface waters at the site. In surface waters, boron, manganese, arsenic, mercury, lead, and zinc all exceed guideline values. Furthermore, reports from the Tasman Solid Waste Permit Application show that leachate is flowing from the waste site towards both the A8 and Urupa ponds, which are outside the boundaries of the landfill area and the lease agreement. Analysis of the soils and waters of these ponds shows that concentrations of arsenic, boron, mercury, lead, and zinc are all orders of magnitude higher than ANZECC guideline levels.

## 3 Methods

For this study, groundwater samples were collected from twenty-six monitoring bores at thirteen locations around and within the landfill area (Figure 2). Each location contains two piezometers, one shallow and one deep. The shallow piezometers are screened across the groundwater table, while the deep ones are installed below the base of the waste site (SKM 2007). The bores are sequentially labeled SKM101 to SKM113, with an 'A' and 'B' suffix tagged to the bore numbers to denote the shallow and deep piezometers, respectively.

### 3.1 Field Collection

Field collection for this study took place in February 2009. In order to minimize cross-contamination, we sampled what we believed to be the most uncontaminated

locations first, followed by the most contaminated. Thus, sampling began at SKM101 near the Western embankment and continued through the waste site towards the Tarawera River. Field blanks were collected at each site and used to ensure that our sampling procedures were not adding to the contamination.

Groundwater samples were obtained using low-flow pumping. This involves pumping the bore at a rate lower than the recharge capacity of the geological material so that turbidity is minimized (SKM 2007). Once groundwater samples were brought to the surface, water was filtered into 60 mL, high-density polyethylene bottles that had been acid washed in preparation for sampling. Trace metal and cation samples were acidified with ultra pure nitric acid immediately after filtration and put on ice within one hour of collection.

Measurements recorded in the field included depth, pH, dissolved oxygen, temperature, and conductivity. A GPS unit was used to record the exact location where the samples were extracted. The time of day, description of the source, and outside conditions were also recorded.

### **3.2 Data Analysis**

Aside from parameters measured in the field, each collected sample was analyzed in the lab for selected ions. The concentrations of major cations were determined by flame atomic absorption spectroscopy (AAS) and the anions by ion chromatography (IC). These analyses were conducted in the geochemistry laboratories at the University of Auckland under the supervision of Dr. Angela Slade.

#### *Atomic Absorption Spectroscopy*

Five cations were measured by atomic absorption spectroscopy: Ca, Mg, Na, K, and Zn. AAS determines cation concentrations by measuring the concentration of photons that are absorbed by a sample. Light is transmitted through a cathode tube designed to receive a specific atom. Variations in photon concentrations change the wavelength of light passing through the sample. This change in wavelength is then used by the AAS to create peak energy absorption readouts. By comparing each atom's degree of absorbance to a calibration curve, sample concentrations can be extrapolated.

#### *Ion Chromatography*

Ionic chromatography was used to determine the concentrations of four selected anions:  $\text{NO}_3$ ,  $\text{SO}_4$ ,  $\text{HCO}_3$ , and  $\text{Cl}$ . During this process, ions are pressurized in a chromatographic column and are absorbed by the column constituents. Separation occurs in the column when the effluent ion extraction liquid runs in. The retention time of each species determines its concentration. By inserting liquid standards of known concentrations, ion concentrations of collected unknowns can be determined. Deionized water is then run through the system to purge the chamber of contaminants. While this machine is effective in measuring concentrations in the ppm range, concentrations lower than this cannot be recorded.

## **4 Results**

The groundwater samples for this study were analyzed for five major cations (calcium, magnesium, sodium, potassium, and zinc) and four anions (chloride, sulfate,

nitrite, and bicarbonate). The groundwater quality data for samples collected from boreholes is presented in Appendix A, with summary statistics shown in Figures 3 and 4 A-E. In the following analysis, the data from these samples is compared to that collected by Sinclair Knight Merz (SKM) in their hydrogeological investigations of the primary solids waste landfill in May/June and October 2006. Comparing the results from these surveys allows us to look at the way nutrients vary spatially, seasonally, and with depth in groundwater across the waste site.

#### **4.1 Seasonally**

As seen in Graphs 3 A-E, cation concentrations remained fairly consistent between the May/June (winter) and October (fall) sampling rounds in 2006. The exception to this rule was zinc, which measured 2.59 ppm at SKM109A in the winter sampling round, but retested significantly lower at this borehole in October. Concentrations of zinc were also elevated at SKM104B in the winter, although zinc was not retested here during the October round. While a few of the zinc concentrations were variable between winter and fall, the majority of the data suggests that there is no significant seasonal variation in cation concentrations. This seasonal analysis does not take into account February data due to the large gap between the 2009 and the 2006 sampling periods.

#### **4.2 Spatially**

There was significant spatial variation in concentration levels across the site. For all ions, concentrations were lowest along the northern boundary of the landfill area at sites 110 and 111. Concentrations were also fairly low near the Western embankment at site 101, although zinc was measured to be 0.081 ppm - over one hundred times higher than the recommended ANZECC level.

Three main bores mark the southern boundary of the waste site: SKM 103, 104, and 105. At site 103, calcium, magnesium, and bicarbonate levels were all very high, while sodium and potassium concentrations were only slightly elevated. At site 104, cation concentrations skyrocketed, with sodium reaching 431 ppm and zinc reaching 2.24 ppm. Both of these concentrations are well over ANZECC standards. Anion concentrations were also elevated at this location, with both chloride and sulfate reaching maximum levels of 309 and 1300 ppm, respectively. While concentrations of calcium, magnesium, zinc, sulfate, and bicarbonate dropped by orders of magnitude at site 105, potassium, sodium, and chloride concentrations remained high. At 375 ppm, sodium was still well above ANZECC levels at this location.

Both SKM 107 and SKM 113 are located more than 50 meters outside the landfill area and near the banks of the Tarawera River. At site 107, calcium, magnesium, chloride, and bicarbonate all reached local maximums in the shallow borehole, although concentrations did comply with ANZECC standards. Site 113, which is located even further from the landfill area, showed elevated concentrations for calcium, magnesium, potassium, sodium, bicarbonate, and chloride. Zinc remained below 0.004 ppm at both locations.

In the middle of the landfill area, site 112 showed high concentration levels for most ions. Calcium reached an absolute maximum in the shallow bore at this site, measuring over 342 ppm. In May/June 2006, zinc concentrations of 0.014 ppm here exceeded ANZECC levels. Magnesium and bicarbonate were also especially high at this site.



### **4.3 With Depth**

There was significant variation in ion concentrations between shallow and deep boreholes, especially at sites 107, 109, and 112. At 107, concentration levels of calcium, magnesium, and bicarbonate in the shallow bore were significantly higher than those in the deep bore. The opposite trend was seen for sodium and chloride concentrations, which were almost twice as high in the deep borehole at this site. At 109, calcium, magnesium, and bicarbonate concentrations more than doubled with depth. At site 112, concentrations for calcium and bicarbonate were much higher in the shallow bore, while magnesium, sodium, potassium, and chloride concentrations were significantly higher with depth.

### **4.4 Over Time**

While groundwater testing at the Tasman waste site has been inconsistent, data from February 2009 allows us to look roughly at the way ion concentrations are changing over time. In general, concentrations from 2006 and 2009 were very consistent. The few exceptions to this trend were with magnesium, sodium, and calcium, which measured significantly lower in 2009 compared to 2006. Chloride concentrations were significantly higher in 2009, with values almost doubling those measured in 2006. This was true for both shallow and deep boreholes, especially at sites 106, 107, 108, 112, and 113.

## **5 Discussion**

While groundwater quality is most obviously related to geology and land use, other factors may also exert influences that can be difficult to discern. An important factor to consider at the Rotooitipaku site is geothermal activity, which is especially prominent along the southern boundary of the site and has the capacity to largely affect the chemical composition of groundwaters. Because different areas of the Tasman waste site are under different stresses, only general inferences can be made from the data. Nevertheless, by compiling data from previous research and looking at trends in ion concentration levels across the site, many strong suggestions can be made regarding the hydrology of this area, the chemicals that have been deposited here, and the long-term effects that this waste site may have.

### **5.1 Seasonally**

In general, ion concentrations remained fairly consistent between the winter and fall sampling rounds. The notable exception to this trend was zinc, which had high concentrations at SKM109A in May/June 2006 but significantly lower concentrations at this bore in October. SKM comments on this discrepancy noting, “there could have been a higher level of dilution occurring within the bore preceding the [October] sampling event (i.e. from “rainfall recharge”)” which would have reduced “an ongoing source of contamination” (SKM 2007). However, because other ions did not show similar dilution patterns in October, it is more likely that the elevated zinc levels in May/June were due to a one-off source of contamination flowing through the bore.

Overall, the majority of the data implies that there is no significant seasonal variation in ion concentrations. This seasonal analysis does not take into account February data due to the large gap between the 2009 and the 2006 sampling periods. Consistent testing over all four seasons should be completed to provide a more accurate account of the way that ion concentrations vary during the year. This monitoring should make sure to

include testing at site 109 in order to help pinpoint possible sources of zinc contamination in this area.

## **5.2 Spatially**

There is significant spatial variation in ion concentrations across the waste site. In general, water taken from sites 110 and 111 along the northern boundary of the landfill had the lowest ion concentrations. Because these boreholes do not encounter waste and are located above the landfill area, the water quality here is “more typical of unmodified groundwater systems” (SKM 2007). Thus, we can conclude that any contamination in these bores is due to natural causes, and can use this data as a base line to compare concentrations found in other locations around the landfill area.

Concentrations were also fairly low near the Western embankment at site 101. This was expected, as the site lies outside the landfill area and opposite the direction of groundwater flow, which is “from west to east towards the Tarawera River” (SKM 2007). While concentrations at this site were low, they were consistently higher than those along the northern boundary. This suggests slight contamination, due to either anthropogenic or geothermal factors. While site 101 is located near geothermal waters, past research also suggests the influence of effluent dumping at this location. Tull supports this point in her thesis, noting the possibility that “contamination [from the landfill area] has spread to land block A8.” (Tull, 2007). She also notes that anthropogenic influences at this site cannot be determined without further testing of organic parameters in the ground and surface waters.

All bores along the southern boundary of the waste site (102, 103, 104, and 105) showed elevated ion concentrations. This was expected, as the area is marked by strong geothermal activity (Allis 1997). While all four sites are located on a fault that feeds hot water to the riverbank springs (SKM 2007), ion concentrations were significantly higher at site 104 than any of the others. This was especially true for sodium, potassium, zinc, chloride, and sulfate. As Table 1 shows, all of these ions are closely associated to contaminants involved with the mill in Kawerau. Sodium is likely to be a product of the sodium hydroxide in the pulping process, as well as the sodium hydrosulfite involved with bleaching. Zinc is a direct product of pulping, while chloride likely comes from chlorinated compounds involved with bleaching and paper manufacture. Sulfates may result from sulfuric and sulfurous acids involved with pulping. These associations, along with the fact that site 104 lies directly in the landfill area, provide evidence that contamination is largely attributed to effluent dumping. Because the dominant flow pattern in this area is lateral, contaminants from these boreholes are likely to flow toward the Tarawera River (SKM 2007).

Although sites 107 and 113 are located outside the landfill area, ion concentrations were elevated at both locations. Both of these sites are located outside the zone of direct geothermal influence, which (according to a mixing ratio analysis performed by SKM in 2007) is greatest near the southern boundary of the landfill area and becomes weak further north. However, because groundwater is shown to flow from west to east across the landfill area, sites 107 and 113 are in the likely pathway of contaminants moving towards the Tarawera River. High ion levels in these bores suggest that contaminants from effluent dumping, geothermal activity, or other influences within the waste site are mobile and actively flowing away from the landfill area. It is very important that consistent monitoring at these boreholes along the Tarawera continue so that the flow of contaminants into the river can be tracked.

SKM112, which is located in the middle of the landfill area, also showed elevated ion concentrations. Sodium and zinc concentrations were both high at this location, suggesting influence from pulping and bleaching wastes. However, the most notable concentration spikes were for calcium, magnesium, and bicarbonate, none of which are directly associated with pollution outputs at the mill. Because the sludge at this location covers what used to be an active hot spring, it is possible that some of this contamination is due to geothermal activity beneath the boreholes. Further study is needed to characterize the groundwater at this site and distinguish between the influences of effluent dumping and geothermal activity.

### **5.3 With Depth**

There was significant variation in ion concentrations between shallow and deep boreholes, especially at sites 107, 109, and 112. At 107, higher concentrations of calcium, magnesium, and bicarbonate in the shallow bore were likely due to inputs from trace waste material and underlying peat. The increase in chloride concentrations with depth indicate mixing with cross-flowing groundwater, as deep thermal waters approach the surface. At site 109, groundwater flow was upwards, meaning the significant increase in calcium, magnesium, and bicarbonate concentrations at depth may have been results of more natural background inputs, such as geothermal waters and buried wetland vegetation. At site 112, most parameters increased with depth. Greater concentrations in the deeper piezometer at this location were likely due to reducing conditions and greater organic sources (e.g. peat, trace roots). Furthermore, since groundwater at this site showed a strong downwards flow, inputs from waste material were likely to be drawn down to the local, underlying groundwater resources. Thus, elevated parameters were attributed to both landfill contamination as well as natural background inputs.

### **5.4 Over Time**

In general, concentrations from 2006 and 2009 are very consistent. While ion concentrations are not changing rapidly, it is important to note that the movement of nutrients, metals, and contaminants through the waste material is extremely slow. It may take decades for contaminants in the waste to be released into the groundwater system. Because of this, consistent testing must be maintained across the landfill area so that changes in groundwater quality can be measured more accurately over an appropriate time scale.

While most ion concentrations have remained consistent, magnesium, sodium, and calcium concentrations have all decreased over the past three years. This could be due to a number of factors, including decreased geothermal activity, increased groundwater recharge, etc. A more specific explanation for this pattern would require a compilation of further studies to look at the way geothermal inputs, precipitation, runoff, evaporation, etc. have changed over the past few years.

Elevated concentrations of chloride in recent years are slightly concerning. Chloride is closely associated with pollution outputs from the mill, notably the chlorinated compounds involved with bleaching and paper manufacture. While waste is now treated to remove most chlorinated compounds before it is dumped, the site at Lake Rotootipaku contains a lot of older, contaminated waste that contains high concentrations of chlorinated compounds. These compounds could be hazardous if released into the Tarawera River or surrounding area. The increases in chloride concentrations over the past three years may indicate that some of these older contaminants have started to leach out of and move

through the waste material. While this is a lofty assumption to make given the limited data we have available, more consistent testing of ground water throughout the waste site is crucial to further monitor these changes.

## 6 Conclusion

Overall, this study was successful in building upon previous site assessments of the Norske Skog waste site to analyze the way selected ions in groundwater vary seasonally, spatially and with depth. While water chemistry remained fairly consistent between seasons, there was significant variation in ion concentrations across the waste site, as well as with depth. Current data also showed that concentrations of some ions have changed significantly since the site assessments in 2006. Given the dynamic nature of the hydrology, geology and related geothermal influences at this site, identifying the sources for this type of change is often difficult. Further testing is needed in order to clear up ambiguity in the data and more accurately distinguish between anthropogenic and geothermal contamination.

Although this study has proven that some contaminants exceed ANZECC guidelines, others were found to be well within the acceptable range for recreational water quality standards. Regardless, the toxic nature of the waste dumped at this site causes concern over the future implications that the waste material may have. Environmental testing at the landfill has been inexcusably inconsistent in the past. With no groundwater studies conducted between 2006 and 2009, finding any reliable trends in the data is very difficult. Thus, it is clear that more consistent monitoring is needed to accurately track elevated concentrations of potentially harmful contaminants. Studies should also work to clarify the specific sources of contamination at different points throughout the waste site so that effective remediation strategies can be implemented. This type of groundwater assessment is crucial for the development of effective protection strategies as well as general water resource planning in the Kawerau area.

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## Appendix A

| <b>Primary Solids Waste Landfill - Hydrological Investigation by SKM</b><br><i>May/June 2006 Groundwater chemistry sampling results</i><br>(all measurements are in ppm) |           |          |          |          |         |          |     |
|--|-----------|----------|----------|----------|---------|----------|-----|
| Borehole ID  | Depth (m) | Ca (ppm) | Mg (ppm) | Na (ppm) | K (ppm) | Zn (ppm) | pH  |
| SKM101A  | 3         | 68.5     | 6.77     | 16.8     | 9.56    | 0.097    | 6.5 |
| SKM101B  | 13.5      | 12.5     | 1.29     | 9.86     | 3.61    | 0        | 6.1 |
| SKM102B  | 22        | 22.4     | 4.51     | 38.2     | 14.8    | 0.081    | 2.9 |
| SKM103A  |           | 159      | 25.9     | 90.7     | 20.6    | 0        | 6.5 |



|          |       |      |      |      |      |       |         |
|----------|-------|------|------|------|------|-------|---------|
| SKM104B  |       | 80.1 | 21   | 431  | 78.6 | 2.24  | 3.2     |
| SKM105B  | 6.325 | 49.5 | 3.8  | 375  | 47.3 | 0     | 6.4     |
| SKM106A  | 5     | 156  | 29.3 | 73.5 | 15.1 | 0     | 6.4     |
| SKM107A  | 6     | 190  | 32.1 | 70.2 | 13.6 | 0.003 | 6.3     |
| SKM107B  | 10    | 25.4 | 8.34 | 142  | 14.8 | 0     | 6.4     |
| SKM 108A | 6.47  | 19.2 | 5.3  | 166  | 26.1 | 0.006 | 6.26    |
| SKM109A  | 9     | 26.4 | 4.71 | 24.8 | 4.74 | 2.59  | 6.31    |
| SKM109B  | 14    | 60.3 | 10.7 | 23.7 | 5.21 | 0     | 6.54    |
| SKM110A  | 6.42  | 8.98 | 3.65 | 8.9  | 3.74 | 0.005 | 5.86    |
| SKM111A  | 6.26  | 3.96 | 3.36 | 9.33 | 2.05 | 0.007 | 5.97    |
| SKM112A  | 8.66  | 302  | 8.38 | 19   | 4.81 | 0.014 | 6.09    |
| SKM112B  | 20.5  | 71.9 | 17.1 | 83.5 | 10.7 | 0.001 | 6.17    |
| SKM 113A | 3.7   | 105  | 16.8 | 38.5 | 10.3 | 0.001 | 6.4     |
| ANZECC   |       | -    | -    | 300  | -    | 0.008 | 6.5-8.5 |

**Table 2. Results of sample analyses of selected major cations for waste site groundwater in May/June 2006. Concentrations exceeding ANZECC levels are highlighted in red. Locations of sample sites are shown in Figure 2.**

| <b>Primary Solids Waste Landfill - Hydrological Investigation by SKM</b> |       |          |         |         |             |
|--|-------|----------|---------|---------|-------------|
| <i>May/June 2006 Groundwater chemistry sampling results</i>              |       |          |         |         |             |
| (all measurements are in ppm)  |       |          |         |         |             |
| Borehole ID  | Depth | Chloride | Sulfate | Nitrite | Bicarbonate |
| SKM101A  | 3     | 4.5      | <0.5    | <0.002  | 287         |
| SKM101B  | 13.5  | 6        | 0.6     | <0.002  | 68          |
| SKM102B  | 22    | 12.5     | 1460    | <0.02   | <1          |
| SKM103A  |       | 22.6     | 25.4    | <0.002  | 808         |
| SKM104B  |       | 309      | 1300    | 0.04    | <1          |
| SKM105B  | 6.325 | 259      | 303     | <0.002  | 348         |
| SKM106A  | 5     | 21.4     | 0.8     | <0.002  | 742         |
| SKM107A  | 6     | 24.9     | <0.5    | <0.002  | 824         |
| SKM107B  | 10    | 68.5     | 1.2     | <0.002  | 371         |
| SKM 108A   | 6.47  | 76       | 2.6     | 0.002   | 562         |
| SKM109A  | 9     | 9.6      | 28      | 0.037   | 123         |
| SKM109B  | 14    | 10.5     | 50      | <0.002  | 216         |
| SKM110A  | 6.42  | 15.5     | 3       | <0.002  | 36          |
| SKM111A  | 6.26  | 5        | 3.8     | <0.002  | 32          |
| SKM112A  | 8.66  | 13.2     | <0.5    | <0.002  | 1020        |
| SKM112B  | 20.5  | 27.8     | <0.5    | 0.007   | 509         |
| SKM113A  | 3.7   | 12.8     | <0.5    | <0.002  | 493         |

**Table 3. Results of sample analyses of selected anions for waste site groundwater in May/June 2006. Locations of sample sites are shown in Figure 2.**

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|--|
| <b>Primary Solids Waste Landfill - Hydrological Investigation by SKM</b> |
|--|

*October 2006 Groundwater chemistry sampling results*

(all measurements are in ppm)

| Borehole ID | Depth (m) | Ca (ppm) | Mg (ppm) | Na (ppm) | K (ppm) | Zn (ppm) | pH      |
|-------------|-----------|----------|----------|----------|---------|----------|---------|
| SKM101A     | 3         | 57.7     | 4.77     | 13.5     | 8.38    | 0.049    | 6.8     |
| SKM106A     | 5         | 164      | 23.8     | 63.8     | 17.9    | 0.001    | 6.3     |
| SKM106B     | 11.5      | 107      | 13.4     | 105      | 12.3    | 0.002    | 6.4     |
| AKM107A     | 6         | 185      | 29.6     | 64.7     | 13      | 0.002    | 6.9     |
| SKM107B     | 10        | 21       | 6.45     | 141      | 14.3    | <0.001   | 6.9     |
| SKM108A     | 6.47      | 19.4     | 4.43     | 148      | 25.5    | 0.004    | 5.7     |
| SKM108B     | 11        | 10.5     | 5.14     | 176      | 17.2    | 0.004    | 5.9     |
| SKm109A     | 9         | 25       | 4.14     | 24.7     | 4.73    | 0.003    | 6.9     |
| SKm109B     | 14        | 59.7     | 10.1     | 23.9     | 5       | 0.003    | 6.9     |
| SKM110A     | 6.42      | 5.34     | 3.95     | 9.3      | 4.22    | 0.005    | 6.8     |
| SKM110B     | 12        | 1.98     | 0.75     | 13.7     | 4.64    | 0.002    | 6.9     |
| SKM111A     | 6.26      | 3.94     | 4.18     | 6.12     | 2.03    | 0.005    | 6.5     |
| SKM111B     | 10.96     | 2.92     | 1.93     | 7.77     | 4.03    | 0.011    | 6.5     |
| SKM112A     | 8.66      | 342      | 8.91     | 20.4     | 5.19    | 0.006    | 6.6     |
| SKM112B     | 20.5      | 79.1     | 18.5     | 88.4     | 11.5    | 0.002    | 6.5     |
| SKM113A     | 3.7       | 111      | 16.8     | 34.5     | 8.84    | 0.001    | 6.6     |
| SKM 113B    | 9         | 30.2     | 13.9     | 142      | 15.6    | 0.004    | 6.6     |
| ANZECC      |           | -        | -        | 300      | -       | 0.008    | 6.5-8.5 |

**Table 4. Results of sample analyses of selected major cations for waste site groundwater in October 2006. Concentrations exceeding ANZECC levels are highlighted in red. Locations of sample sites are shown in Figure 2.**

**Primary Solids Waste Landfill - Hydrological Investigation by SKM**

*October 2006 Groundwater chemistry sampling results*

(all measurements are in ppm)

| Borehole ID | Depth (m) | Chloride | Sulfate | Nitrite | Bicarbonate |
|-------------|-----------|----------|---------|---------|-------------|
| SKM101A     | 3         | 4.44     | <0.5    | <0.002  | 235         |
| SKM106A     | 5         | 21.1     | <1      | 0.004   | 928         |
| SKM106B     | 11.5      | 52.1     | 2       | <0.002  | 766         |
| AKM107A     | 6         | 21.8     | <0.5    | ,0.01   | 1040        |
| SKM107B     | 10        | 76.5     | 1.2     | <0.002  | 407         |
| SKM108A     | 6.47      | 81.5     | 3.4     | 0.006   | 625         |
| SKM108B     | 11        | 128      | 6.5     | 0.007   | 444         |
| SKm109A     | 9         | 10.2     | 25      | 0.011   | 125         |
| SKm109B     | 14        | 10.8     | 48.3    | <0.002  | 230         |
| SKM110A     | 6.42      | 21.7     | 3.9     | <0.002  | 21          |
| SKM110B     | 12        | 11.7     | 4       | <0.002  | 26          |
| SKM111A     | 6.26      | 7.2      | 3.3     | <0.002  | 19          |
| SKM111B     | 10.96     | 5.6      | 6.6     | <0.002  | 25          |
| SKM112A     | 8.66      | 13.9     | <0.5    | <0.002  | 1090        |

|         |      |      |      |        |     |
|---------|------|------|------|--------|-----|
| SKM112B | 20.5 | 27.5 | <0.5 | <0.002 | 556 |
| SKM113A | 3.7  | 13.4 | <0.5 | 0.003  | 563 |
| SKM113B | 9    | 55.5 | <0.5 | <0.002 | 533 |

**Table 5. Results of sample analyses of selected major anions for waste site groundwater in October 2006. Locations of sample sites are shown in Figure 2.**

| <b>Primary Solids Waste Landfill - Hydrological Investigation by FA</b> |           |          |          |          |         |          |         |
|---|-----------|----------|----------|----------|---------|----------|---------|
| <i>February 2009 Groundwater chemistry sampling results</i>             |           |          |          |          |         |          |         |
| (all measurements are in ppm)   |           |          |          |          |         |          |         |
| Borehole ID   | Depth (m) | Ca (ppm) | Mg (ppm) | Na (ppm) | K (ppm) | Zn (ppm) | pH      |
| SKM101A   | 3         | 2.152    | 6.619    | 32.049   | 20.567  | 0.038    | 6.69    |
| SKM101B   | 13.5      | 0.794    | 1.269    | 18.909   | 3.124   | ND       | 6.75    |
| SKM106A   | 5         | 4.176    | 24.21    | 21.476   | 19.083  | 0.116    | 6.28    |
| SKM106B   | 11.5      | 48.282   | 10.575   | 27.253   | 13.269  | 0.011    | 6.08    |
| SKM107A   | 6         | 2.576    | 25.075   | 49.355   | 13.176  | ND       | 6.28    |
| SKM107B   | 10        | 2.076    | 4.06     | 44.061   | 13.782  | ND       | 6.14    |
| SKM108A   | 6.47      | 8.183    | 6.167    | 47.924   | 15.252  | 0.053    | 6.31    |
| SKM108B   | 11        | -0.655   | 3.016    | 56.613   | 20.732  | 0.038    | 6.34    |
| SKM109A   | 9         | 9.832    | 4.484    | 40.172   | 7.22    | 0.095    | 6.48    |
| SKM109B   | 14        | 18.34    | 5.884    | 31.958   | 6.21    | ND       | 7.11    |
| SKM110B   | 12        | ND       | 0.258    | 21.507   | 3.517   | ND       | 8.83    |
| SKM111A   | 6.26      | ND       | ND       | n.a.     | n.a.    | 0.006    | 8.02    |
| SKM111B   | 10.96     | ND       | 1.288    | 15.206   | 3.53    | ND       | 5.47    |
| SKM112A   | 8.66      | ND       | ND       | n.a.     | n.a.    | ND       | 6.28    |
| SKM112B   | 20.5      | 23.154   | 13.751   | 51.674   | 10.937  | 0.035    | 6.98    |
| SKM113A   | 3.7       | High     | 18.612   | 45.062   | 10.565  | ND       | 6.25    |
| SKM113B   | 9         | 6.202    | 9.125    | 38.839   | 14.92   | 0.007    | 6.41    |
| ANZECC  |           | -        | -        | 300      | -       | 0.008    | 6.5-8.5 |

**Table 6. Results of sample analyses of selected major cations for waste site groundwater in February 2009. Concentrations exceeding ANZECC levels are highlighted in red. Locations of sample sites are shown in Figure 2.**

| <b>Primary Solids Waste Landfill - Hydrological Investigation by FA</b> |           |          |          |         |             |
|---|-----------|----------|----------|---------|-------------|
| <i>October 2006 Groundwater chemistry sampling results</i>              |           |          |          |         |             |
| (all measurements are in ppm)   |           |          |          |         |             |
| Borehole ID   | Depth (m) | Chloride | Sulfate  | Nitrite | Bicarbonate |
| SKM101A   | 3         | 16.8528  | 109.4592 | n.a.    | n.a.        |
| SKM101B   | 13.5      | 16.1624  | 1.0101   | n.a.    | n.a.        |
| SKM106A   | 5         | 65.2824  | n.a.     | 4.9112  | 65.2824     |
| SKM106B   | 11.5      | 99.517   | n.a.     | n.a.    | 99.517      |
| SKM107A   | 6         | 63.9817  | n.a.     | n.a.    | 63.9817     |

|         |       |          |         |         |         |
|---------|-------|----------|---------|---------|---------|
| SKM107B | 10    | 173.8176 | n.a.    | n.a.    | n.a.    |
| SKM108A | 6.47  | 84.1653  | 1.1377  | n.a.    | n.a.    |
| SKM108B | 11    | 331.6143 | 15.0707 | n.a.    | n.a.    |
| SKM109A | 9     | 52.2325  | 31.0729 | 9.6003  | n.a.    |
| SKM109B | 14    | 27.2519  | 4.3006  | 7.4332  | n.a.    |
| SKM110A | 6.42  | n.a.     | n.a.    | n.a.    | n.a.    |
| SKM110B | 12    | 27.575   | 8.1277  | 5.78    | n.a.    |
| SKM111A | 6.26  | n.a.     | n.a.    | n.a.    | n.a.    |
| SKM111B | 10.96 | 16.5119  | 15.6401 | 21.1768 | n.a.    |
| SKM112A | 8.66  | n.a.     | n.a.    | n.a.    | n.a.    |
| SKM112B | 20.5  | 55.8382  | 6.7553  | 7.1637  | n.a.    |
| SKM113A | 3.7   | 49.4508  | n.a.    | n.a.    | 49.4508 |
| SKM113B | 9     | 109.3519 | n.a.    | n.a.    | n.a.    |

**Table 7. Results of sample analyses of selected major anions for waste site groundwater in February 2009. Locations of sample sites are shown in Figure 2.**