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**Abstract**

Scrap tires are being recycled into many products in order to bypass slow degradation in landfills. Recycled rubber tire mulch contains zinc oxide used in tire formation that can be released through the creation of leachates. This study examines the relationship between temperature environment and leachate zinc concentration. After observing rubber mulch surface temperatures in conjunction with other factors, it was hypothesized that higher temperatures would lead to increased zinc release by rubber mulch and higher leachate zinc concentrations. Leachates were created by mixing 10 grams of mulch and 200 mL distilled water and placing in 5ºC, 29ºC, and 71ºC environments for 24 hours. Zinc content in ppm was then tested and statistically analyzed with ANOVA at alpha=0.05. A significant decrease in mean leachate zinc concentration as temperature increased was shown between the 29ºC ($M = 5.733$, $SD = 1.486$) and 71ºC ($M = 4.133$, $SD = 0.516$) treatments and the 5ºC ($M = 6.533$, $SD = 0.743$) and 71ºC treatments ($F(2, 42) = 22.19$, $p < 0.01$). Therefore, within these intervals, decreasing temperatures increased rubber mulch breakdown and leachate zinc concentration. Because tires are created at high temperatures during the vulcanization process, it is reasonable to consider that tires are strongest at higher temperatures. Studying the effect of rubber mulch leachates on soil and various organisms would provide a direct study to more accurately deduce potential environmental impacts.

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Scrap tires are being recycled into many products in order to bypass slow degradation in landfills. Recycled rubber tire mulch contains zinc oxide used in tire formation that can be released through the creation of leachates. This study examines the relationship between temperature environment and leachate zinc concentration. After observing rubber mulch surface temperatures in conjunction with other factors, it was hypothesized that higher temperatures would lead to increased zinc release by rubber mulch and higher leachate zinc concentrations. Leachates were created by mixing 10 grams of mulch and 200 mL distilled water and placing in 5ºC, 29ºC, and 71ºC environments for 24 hours. Zinc content in ppm was then tested and statistically analyzed with ANOVA at alpha=0.05. A significant decrease in mean leachate zinc concentration as temperature increased was shown between the 29ºC ($M = 5.733$, $SD = 1.486$) and 71ºC ($M = 4.133$, $SD = 0.516$) treatments and the 5ºC ($M = 6.533$, $SD = 0.743$) and 71ºC treatments ($F(2, 42) = 22.19$, $p< 0.01$). Therefore, within these intervals, decreasing temperatures increased rubber mulch breakdown and leachate zinc concentration. Because tires are created at high temperatures during the vulcanization process, it is reasonable to consider that tires are strongest at higher temperatures. Studying the effect of rubber mulch leachates on soil and various organisms would provide a direct study to more accurately deduce potential environmental impacts.

## Introduction

Tires are a major source of solid waste worldwide. The S.C. Department of Health and Environmental Control estimates that 4.5 million scrap tires are produced annually by South Carolina alone.[1] In fact, sixty-five percent of all scrap rubber comes from old tires.[2] When tires are no longer able to be used, they are often thrown into landfills and left to degrade slowly. In addition to being unattractive, tires left in landfills are classified as fire hazards, health hazards, and even environmental pollutants. To prevent used tires from filling up landfills, scientists are researching ways to best reuse and recycle tires. The rubber, steel, and fiber in tires are repurposed in a variety of industries. Most recycled rubber is ground into fine pieces called crumb rubber. Some of crumb rubber's uses include as an ingredient in rubber-modified asphalt and as an artificial turf infill, or soil substitute. Other old tires are shredded into larger pieces to make rubber tire mulch. An alternative to wood mulch, rubber mulch is used commonly in playgrounds, gardens, and yards.

The use of rubber mulch in playgrounds and gardens places it into direct contact with the outdoor environment. Direct sunlight causes the rubber to heat to high surface temperatures. These high temperatures can exceed those of the surrounding air temperature and cause a fire hazard. This is a concern especially in areas such as South Carolina where it is hot for long periods of time. Very high temperatures can even alter the structure of rubber.[2] In an urban heat island simulation by Yaghoobian, Kleissl, and Krayenhoff, the use of crumb rubber infilled athletic turf increased surrounding air temperatures.[3] Irrigation lowered the surface temperatures of crumb rubber infilled athletic fields for about 200 minutes.[4] However, irrigation still resulted in higher field surface temperatures than unirrigated grass areas. Furthermore, leachates obtained from crumb rubber infill athletic fields at higher temperatures demonstrated more mutagenic potential towards bacteria than those obtained at lower temperatures.[5] These results introduce a possible correlation between rubber mulch temperature and its release of water soluble agents.

Leachates occur when water drains through a substance, carrying dissolved or suspended parts of the substance with it. Outdoors, rain drains through rubber mulch and creates leachates. These leachates carry water soluble agents from the mulch into the soil, where these agents can change soil properties and be accumulated by plants or other organisms. Thus, the process of leaching enables rubber mulch to have widespread and possibly harmful environmental effects. Leachates were created in a study by Dorsey et al. by mixing crumb rubber samples with distilled water. The leachates demonstrated mutagenic potential towards bacteria due to harmful chemicals that leached out of the crumb rubber.[5]

As rubber tire mulch degrades, it has the potential to release zinc. Zinc is present in tires in the form of zinc oxide, which is added during manufacturing to strengthen the tires.[2] Zinc oxide consists of only about one percent of a car tire's total composition.[6] However, recycled tire products can release this zinc, as is demonstrated in many studies.[7-9] In each study, zinc soil levels increased after recycled rubber products were mixed with the soil. In turn, increased zinc soil levels increased zinc concentrations in plant tissue.[10] Recycled rubber products also can release other potentially hazardous substances such as polycyclic aromatic hydrocarbons, lead, chromium, and cadmium.[11-12]

The zinc released in the studies above can be helpful or harmful depending on the amount released and the surrounding environmental conditions. In zinc-deficient soil, ground tire rubber is effective as a slow-release zinc fertilizer, with equivalent or better results than those of commercial fertilizers.[9] The application of zinc solutions to the soil and foliage of rice plants increases both rice plant yields and plant tissue zinc concentrations.[10]

On the other hand, zinc toxicity occurs in plants and animals when levels of zinc are too high. Symptoms of zinc toxicity in plants include reduced plant and root growth and smaller leaf size.[13] In an experiment by Khoshgoftarmanesh, Eshghizadeh, and Chaney, tomato plants grown with crumb rubber as a soil medium exhibited low yields and growth due to zinc toxicity.[8] Plant tissue zinc concentrations exceeding 200 parts per million can lead to zinc toxicity in plants; however, the level at which zinc toxicity may occur can be different among plants depending on how the plants accumulate zinc.[14] In a study by Zalewska and Nogalska, the yield of sunflower plants decreased once 200 milligrams of zinc were added per kilogram of soil.[15] Yet, in white mustard plants, plant yield and growth did not decrease until 400 milligrams of zinc were added per kilogram of soil.[15] Zinc toxicity can be harmful to other organisms. High levels of zinc decreased the maximum and mean lifespan of *Caenorhabditis elegans* in an experiment by Kumar et al. and lowered algae protein, chlorophyll, carbohydrate, starch, and amino acid levels in a study by Mane, Kadam, and Bhosle.[16-17] The extent of organic compound limitation in the algae depended on zinc concentration and the type of algae, while the lifespan decrease in *C. elegens* depended on the age of the worm when exposed to the zinc. Therefore, the point at which zinc toxicity can occur and be harmful to an organism depends on the species as well as many other factors.

One way to prevent rubber-caused zinc toxicity is by acid-washing rubber with nitric acid to remove excess zinc.[8] Acid-washing rubber products could prevent zinc leaching when implemented in the environment.[8] However, the rubber acid-washing process produces leachates that have high levels of zinc.[18] These zinc-rich leachates can be used as a zinc fertilizer but could be harmful if released.[18]

The purpose of this experiment was to determine whether the temperature at which rubber mulch leachates are created has an effect on the zinc concentration of the leachates. This study discusses the observed interaction between sun exposure and rubber mulch surface temperature and examines the relationship between temperature environment and zinc concentrations in rubber mulch leachates. Information concerning zinc leaching from rubber mulch aids in preventing unhealthy increases in soil and plant zinc levels that can damage the environment.

It was hypothesized that increased sun exposure would lead to higher rubber mulch surface temperatures. In addition, mulch surface temperatures were hypothesized to be higher than air and grass surface temperatures. It was also hypothesized that higher temperatures would lead to increased zinc release by rubber mulch and therefore higher zinc concentrations in the leachates.

The experiment was conducted in two phases. In the preliminary phase, rubber mulch was spread evenly across an outdoor area. The surface temperatures of both the rubber mulch and a grass control were recorded in addition to air temperature, sun exposure, and time of day. In the experimental phase, vessels of rubber mulch and water were kept in an incubator or refrigerator at different temperatures. The resulting leachates were then tested for their zinc concentration.

## Methods

Prior to experimentation, mulch surface temperatures were recorded during summer afternoons in conjunction with air temperatures and sun exposure. The highest mulch surface temperature recorded was 81.9 degrees Celsius on a sunny day of 37 degrees Celsius; the lowest temperature recorded was 39.0 degrees Celsius on a cloudy day of 35 degrees Celsius. The results of the preliminary observations were considered in the formulation of hypotheses. Additional preliminary studies were then conducted to determine the temperature and time at which zinc was measurable in the mulch leachate. The treatment temperatures, in degrees Celsius, were determined in part based on these results.

A new bag of mulch was opened and mixed in a box in order to allow differently sized pieces of mulch to spread evenly throughout the box. Mulch was scooped out of the box, measured into 10 gram amounts using a triple beam balance, and placed in a numbered Ziploc bag. This process was repeated until 45 bags were filled with the mulch samples. The 45 numbered bags were split into 3 groups, allotting 15 samples for each temperature level, using a random number generator to achieve a random sample. The sample bags were then relabeled with their group and number, such as 2-8. In order to create the leachates, fifteen 250 mL flasks were labeled corresponding to each sample. The flasks were filled with 200 milliliters of distilled water and then with the corresponding bag of mulch, using a funnel. The flasks were then placed in the temperature environment of their assignment: the refrigerator or incubator. After 24 hours, the flasks were removed from the environment and allowed to cool to room temperature using a water bath. Once cool, a mesh strainer was used to filter the leachates out of the flasks and into corresponding labeled beakers. This separated the leachate from the mulch, which was disposed of as non-hazardous waste. Beakers of leachates were covered with Parafilm until zinc testing. These procedures were conducted using samples for each temperature: 5, 29, and 71 degrees Celsius.

Zinc concentrations in the leachates were determined using the procedures from the Zinc Test Kit ordered from LaMotte.[19] Since leachates were considerably below 200 milliliters upon removal from their temperature environment in the 71 degree treatment, distilled water was added until each leachate was 200 milliliters in volume. Throughout leachate testing for zinc concentrations, safety precautions were used, including wearing safety goggles, gloves, and a lab coat to prevent contact with the skin, eyes, nose, or mouth by the leachates. The zinc testing was conducted in a well- ventilated area to prevent inhalation of the reagents. For disposal, leachates were flushed down the drain with water. Data were analyzed at alpha equal to 0.05 with an ANOVA test.

## Results

Zinc concentrations were recorded in parts per million for each leachate, and 15 leachates were tested for each treatment. The mean zinc concentration of the leachates kept at 5 degrees Celsius was 6.533 ppm, with a standard deviation of 0.743 ppm. Results for this treatment ranged from 5 to 7 ppm. Leachates kept at 29 degrees Celsius had a lower mean zinc concentration of 5.733 ppm, but a larger standard deviation of 1.486 ppm and a higher range from 4 to 9 ppm. The zinc concentration of leachates kept at 71 degrees Celsius ranged from 3 to 5 ppm, with a mean of 4.133 ppm and a standard deviation of 0.516 ppm. Each individual zinc concentration value is located in the appendix and a descriptive summary of the results is located in Table 2. Figure 2 shows each individual value of zinc concentration for each leachate plotted corresponding to the leachates' temperature environment. In general, zinc concentration means decreased as temperature of treatment increased.

Data were determined to be relatively normal, so an ANOVA test was used to compare the 5, 29, and 71 degree treatments. Since $p<0.001$ and is less than the alpha value of 0.05, the null hypothesis was rejected, indicating a significant difference between at least one of the treatment groups in zinc concentration ($F(2, 42) = 22.19$, $p< 0.01$). The ANOVA summary can be found in Table 3. A Tukey test was conducted that indicated significant differences found between the 5 degree and 71 degree treatments and between the 29 degree and 71 degree treatments; there was no significant difference found between the 5 degree and 29 degree treatments.

## Discussion

Rubber mulch leachates were created in different temperature environments in order to examine the relationship between temperature environment and leachate zinc concentration. Preliminary study supported the hypothesis that increased sun exposure increases rubber mulch surface temperature, reaching temperatures higher than the air or grass surfaces. In light of this information, it was hypothesized that higher temperatures would increase rubber zinc release and cause higher zinc concentrations in rubber mulch leachates. The data displayed above does not support this hypothesis, as the lowest mean leachate zinc concentration was observed at the highest tested temperature of 71 degrees Celsius (Table 2; Figure 2).

The overall decrease in mean leachate zinc concentration as temperature increased suggests that decreasing temperatures increases rubber mulch breakdown and, consequently, increases zinc transferred to the leachates (Figure 2). However, the data demonstrate a significant decrease in leachate zinc concentration (Table 6) between the 29 and 71 degrees Celsius treatments and the 5 and 71 degrees Celsius treatments ($F(2, 42) = 22.19$, $p< 0.01$) that does not occur between the 5 and 29 degrees Celsius treatments (Table 5). This may imply that rubber mulch degradation levels off at a certain point. It may also be possible that the 24-degree temperature interval between 5 and 29 degrees Celsius, near half of the temperature interval between 29 and 71 degrees Celsius, was not wide enough to contain a significant change in zinc release within that interval. This assumes that the change in zinc release would have been so gradual as to be considered more significant over a wider temperature interval, and also assumes that the relationship between temperature and leachate zinc concentration was linear. However, there is not enough evidence to substantiate a linear model, and more temperatures would have to be tested to draw any more conclusions as to the validity of these hypotheses.

In the preliminary study, rubber mulch consistently exhibited higher surface temperatures than a grass control. These results are consistent with the simulation conducted by Yaghoobian, Kleissl, and Krayenhoff, in which simulated grass surface temperatures showed lower surface temperatures than artificial turf, which contains crumb rubber.[3] The fact that zinc was able to be extracted from rubber mulch in a distilled water solution relates to the study by Khoshgoftarmanesh, Taheri, Shariatmadari, Ghaziaskar, and Chaney where zinc was extracted from ground tire rubber in various acid solutions.[10] Zinc in distilled water leachates in this study was present in much smaller concentrations than in the acid leachates, but was nevertheless able to be extracted by the non-acidic distilled water. This was also the case in a study by Zhang, Han, Zhang, and Crain where zinc was observed in large amounts in crumb rubber after its digestion by nitric acid.[12] Significantly higher amounts of zinc detected in ground and crumb rubber in studies by Zhang, Han, Zhang, and Crain and by Taheri, Khoshgoftarmanesh, Shariatmadari, and Chaney can be partially attributed to the fact that these forms of rubber have higher surface areas and therefore more potential for the release of zinc.[9, 12]

Overall, temperature treatment did have an effect on rubber mulch breakdown and, consequently, leachate zinc concentration between 29 and 71 degrees Celsius and between 5 and 71 degrees Celsius. Within these stated temperature intervals, mean leachate zinc concentration increased as temperatures decreased, which suggests increasing rubber mulch breakdown as temperatures within these intervals decreased. The lower concentration of harmful substances of leachates created at higher temperatures is not in keeping with the results of Dorsey et. al's study, where crumb rubber leachates created at higher temperatures showed more mutagenic potential based on contents of mutagenic water soluble agents.[5] This disparity may be due to the different properties of crumb rubber and rubber mulch or the different properties of zinc and the mutagenic agents.

During the vulcanization process, rubber and other tire ingredients heat to high temperatures in order to create more durable and elastic tires.[2] In addition, friction between the tires and the road as vehicles move can heat up tires during their use. For these reasons, it is reasonable to consider that tires are created so that they are their strongest at higher temperatures. This provides a possible explanation for the lower zinc concentrations and presumably reduced rubber tire mulch degradation of leachates created at 71 degrees Celsius as compared to leachates created at 5 and 29 degrees Celsius.

The results of this study introduce possibly serious environmental implications. Leachates can be created as rainwater drains through rubber mulch implemented in the outdoor environment; the leachates can then spread through soil, be accumulated by plants, or find their way into the food or water supply of other organisms. The potential environmental impact of these leachates, whether harmful or otherwise, are difficult to predict due to the different thresholds of zinc toxicity for each organism or habitat shown in the studies of Zalewska and Nogalska, Kumar et al. and Mane, Kadam, and Bhosle regarding sunflowers, white mustard plants, *C. elegans* and algae.[15-17] Due to the comparatively low levels of zinc in the leachates of this study, environmental impacts would most likely be minimal, but cannot be accurately predicted without a more specific context.

This study was not able to be fully controlled due to the variability found within the rubber tire mulch of any given sample or bag of rubber tire mulch. Variables could have been further limited by sorting mulch pieces by size, but this was outside the time constraints of this study. The assumption that each sample of mulch was representative of the population was made in this study. While variation in terms of range and standard deviation was similar between the 5 and 71 degree treatments (Table 2), wider variation demonstrated by the higher range and standard deviation of the 29 degrees Celsius treatment can be attributed to the fact that no distilled water was added to leachates in this treatment to make up for evaporation. Adding distilled water to leachates under 200 milliliters would most likely have reduced the variation and improved the technique of the 29 degrees Celsius treatment.

Additional testing of a wider variety of temperature treatments would provide more insight into the connection between leachate creation temperature and zinc concentration. This includes testing the creation of leachates below 0 degrees Celsius, in freezing temperatures, to relate to colder environments. In addition, zinc concentrations could be tested for leachates made from acid-washed rubber mulch to determine whether acid -washing is a viable solution for the zinc leaching. The study of the effect of rubber mulch leachates on soil and various organisms would provide a direct comparison to accurately deduce possible environmental impacts.

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**Figure 1**

**Hypothesis:** Higher temperatures will lead to increased zinc release by rubber mulch and therefore higher zinc concentrations in the leachates.

**IV:** temperature of the environment in degrees Celsius

| 5 degrees Celsius | 29 degrees Celsius | 71 degrees Celsius |
|---|---|---|
| 15 trials | 15 trials | 15 trials |

**DV:** zinc concentration of the leachate in parts per million

**Control:** distilled water

**Constants:** water composition, rubber to water ratio, equipment used, type of mulch, age of mulch, vessels used, time of exposure

**Table 1. Leachate zinc concentrations in parts per million for each temperature treatment**

| | Zinc concentration (ppm) | | |
|---|---|---|---|
| Trial (Leachate #) | 5 degrees Celsius | 29 degrees Celsius | 71 degrees Celsius |
| 1 | 5 | 7 | 3 |
| 2 | 7 | 4 | 5 |
| 3 | 7 | 5 | 5 |
| 4 | 7 | 5 | 4 |
| 5 | 7 | 6 | 4 |
| 6 | 7 | 6 | 4 |
| 7 | 6 | 5 | 4 |
| 8 | 5 | 9 | 4 |
| 9 | 7 | 5 | 4 |
| 10 | 6 | 5 | 4 |
| 11 | 7 | 5 | 4 |
| 12 | 7 | 5 | 4 |
| 13 | 7 | 9 | 5 |
| 14 | 7 | 5 | 4 |
| 15 | 6 | 5 | 4 |

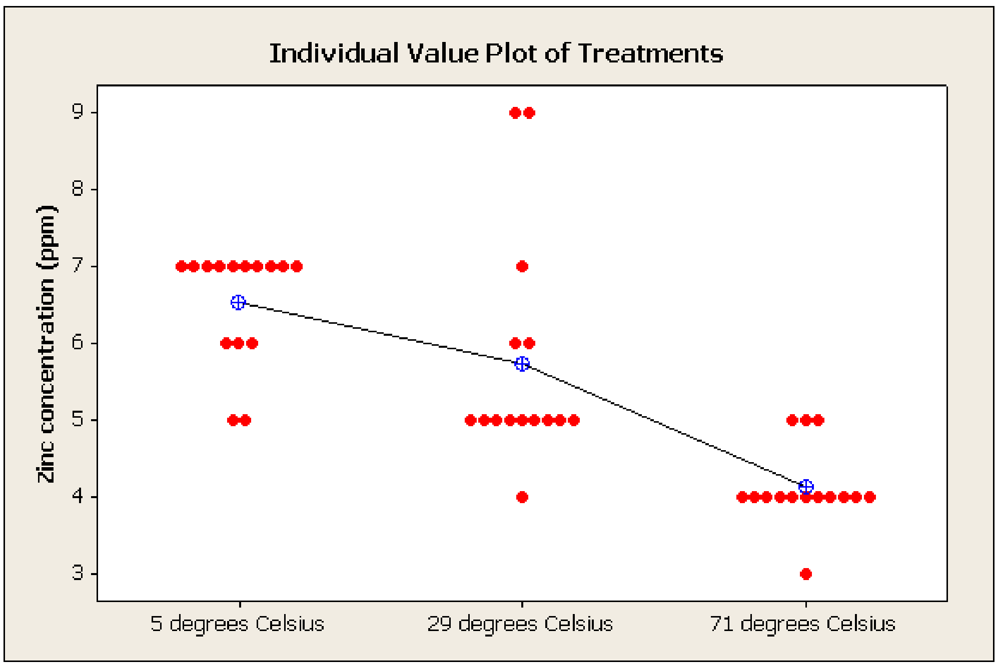
Fifteen trials were completed for each treatment: 5, 29, and 71 degrees Celsius. Zinc concentrations are in parts per million of leachate. Compare to the “control” of distilled water, with a zinc concentration of 0 parts per million. Zinc concentrations for the 5 degree treatment ranged from 5 to 7 ppm. The 29 degree treatment exhibited leachate zinc concentrations ranging from 4 to 9 ppm, while the 71 degree treatment leachates ranged from 3 to 5 ppm of zinc.

**Table 2. Mean, range, and standard deviation of zinc concentrations for each treatment in ppm**

| Treatment | Mean | Range | Standard Deviation |
|---|---|---|---|
| 5 degrees Celsius | 6.533 | 2.000 | 0.743 |
| 29 degrees Celsius | 5.733 | 5.000 | 1.486 |
| 71 degrees Celsius | 4.133 | 2.000 | 0.516 |

The 5 degrees Celsius treatment had the highest mean of 6.533 ppm, followed by 29 degrees Celsius and 71 degrees Celsius with means of 5.733 ppm and 4.133 ppm, respectively. The 29 degree treatment showed the highest range and standard deviation, 5.000 ppm and 1.486 ppm, respectively. Both the 5 and 71 degree treatments exhibited ranges of 2.000 ppm and had standard deviations of 0.743 ppm and 0.516 ppm, respectively.

**Figure 2. Individual value plot of zinc concentration results for each treatment**




Each red dot indicates a value in ppm of zinc of leachates formed at each treatment. Means are connected by a solid line. The mode for the 5, 29, and 71 degree treatments were 7, 5, and 4 ppm, respectively. Values for the 29 degree treatment vary most widely between 4 and 9 ppm. The mode of 7 ppm for the 5 degree treatment was also the highest value recorded for that treatment. Generally speaking, the mean of each treatment decreased as temperature treatments increased in degrees Celsius.

**Table 3. ANOVA Summary table for the 5, 29, and 71 degree treatments**

| Source | DF | SS | MS | F | P |
|---|---|---|---|---|---|
| Factor | 2 | 44.80 | 22.40 | 22.19 | <0.001 |
| Error | 42 | 42.40 | 1.01 | | |
| Total | 44 | 87.20 | | | |

An ANOVA test was used as data were determined to be relatively normal; data were analyzed at alpha equal to 0.05. The null hypothesis, which stated that no significant difference was found between the treatments, was rejected because p<alpha ($F(2, 42) = 22.19$, $p < 0.01$), indicating a significant difference in at least one treatment temperature group.

**Table 4. Descriptive statistics for 5, 29, and 71 degrees Celsius treatment zinc concentrations**

| | N | Mean | SE Mean | StDev | Minimum | Q1 | Median | Q3 | Maximum |
|---|---|---|---|---|---|---|---|---|---|
| 5$^o$C | 15 | 6.533 | 0.192 | 0.743 | 5.000 | 6.000 | 7.000 | 7.000 | 7.000 |
| 29$^o$C | 15 | 5.733 | 0.384 | 1.486 | 4.000 | 5.000 | 5.000 | 6.000 | 9.000 |
| 71$^o$C | 15 | 4.133 | 0.133 | 0.516 | 3.000 | 4.000 | 4.000 | 4.000 | 5.000 |

**Table 5. Tukey test for zinc concentration differences between 5, 29, and 71 $^o$C treatments**

| Comparison | Tukey (q) Value | Conclusion |
|---|---|---|
| 29$^o$C - 5$^o$C | -3.083 | Fail to reject $H_0$ |
| 71$^o$C - 5$^o$C | -9.249 | Reject $H_0$ |
| 71$^o$C - 29$^o$C | -6.166 | Reject $H_0$ |
| Critical Value | 3.44 | |

The absolute value of the Tukey (or q) value of each temperature comparison was compared to the critical value in order to determine the conclusion. Since 3.083 is less than 3.44, the null hypothesis failed to be rejected, indicating no statistical difference between the 5 and 29 degrees Celsius treatments. However, both 9.249 and 6.166 were greater than 3.44, rejecting the null hypothesis, showing a significant difference between the 5 and 71-degree treatments and the 29 and 71-degree treatments.