Zeolite: an Emerging Tool for Mine Reclamation

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Abstract

Tailings sites left from mining operations contain heavy metals which have the potential to bioaccumulate and leech into the surrounding soil and watersheds. Although some heavy metals are essential for biological processes, higher concentrations can be toxic and negatively impact nearby ecosystems and human health. Current tailings reclamation processes are often insufficient in preventing heavy metal bioaccumulation or too expensive and time demanding to be realistically incorporated into mine reclamation strategies. Absorbent porous minerals have been used in industrial wastewater management to remove contaminants. In this study we used one such absorbent mineral, zeolite, to test its ability in neutralizing lead, arsenic and cadmium metals in gold and copper mine tailings. We compared three different concentrations of zeolite in tailings soil and the subsequent effects on plant growth. Although treatment differences in plant biomass was not statistically significant, forthcoming data on heavy metal uptake by the plants will offer more detailed information on the zeolites affect on plant growth.

1. Introduction

As humans expand the demand for mined materials, land reclamation following closure of mineral mines becomes more important. Two gold and copper mines near Kamloops, British Columbia (BC) are situated near grazing land for cattle ranchers. These mine sites are important future grasslands for cattle ranchers, therefore mines must mitigate the negative impacts that tailings facilities may have on grazing cattle, as well as native plant and animal populations, after the mine closes down. Copper and gold mines create tailings ponds to collect chemicals and metals leftover from ore processing. This leads to contained tailings ponds that are rich in heavy metals such as lead, arsenic and cadmium that have the potential to leach into the surrounding environment. If heavy metal leaching does occur, plants can accumulate high levels of heavy metals which then can bioaccumulate up the food chain and are concentrated in animal tissues leading to possible neurological issues and problems with reproduction (Järup, 2003; Fashola et al., 2016). Because of these risks, mine reclamation is a process required by law in order to properly immobilize heavy metals and return the land to its natural, or ecologically equivalent, state.

Not only is mine reclamation very time consuming and expensive, the process is unique to every mine. Depending on the topography of the area, the type of ore being mined and the chemical extraction method used, the mine tailings will have different constitutions; therefore, different reclamation strategies are required (Tailings Management at Natural Resources Canada, 2017). A commonality between mining reclamation strategies is the emphasis placed on neutralizing heavy metals. Currently, many mine tailings reclamation strategies involves pumping the chemicals found in tailings ponds deep into the ground and then capping the disposed chemicals with earth and water, creating a lake. These layered cover systems, although effective, can take many years and tens of thousands of dollars to complete (Callery & Courtney, 2015). Therefore,

research is continually being done to find new ways to make the process of reclamation faster and more efficient.

In this study we used an adsorbent mineral, zeolite, in an attempt to neutralize heavy metals present in tailings soils. Zeolite is a volcanic mineral found in sediment layers. This adsorbent porous mineral has already been used in municipal and industrial wastewater treatment to remove contaminants such as excess nitrogen. Zeolite was also found to be effective at neutralizing lead in slightly acidic garden soil (Wei-yu et al., 2009). The unique quality of zeolite in retaining adsorbed particles makes it more effective for reclamation and treatment than other minerals like vermiculite or pumice (Panuccio et al., 2009). It was theorized that increasing concentrations of zeolite in mine tailings soils would result in decreasing heavy metal content in plants grown in amended tailings. Because zeolite has been noted to be more effective at absorbing chemical cations in acidic conditions, the more acidic tailings would theoretically show better heavy metal uptake and retention in zeolite than alkaline tailings (Guo et al., 2013; Panuccio et al., 2009).

To test the conditions of pH and zeolite concentration, zeolite was added in two different concentrations to totes filled with tailings collected from an open pit copper mine. The tailings were slightly alkaline to begin with, therefore phosphoric acid was added to lower the pH in half of the tailings totes. Two species of plants were grown; bluebunch wheatgrass (*Pseudoroegneria spicata*) and field locoweed (*Oxytropis campestris*) in tailings with low and high concentrations of zeolite as well as tailings with no zeolite all of which were replicated in alkaline and slightly acidic conditions. The plants were grown in pots in the greenhouse over the summer, and harvested afterwards which were then dried, weighed and analyzed for heavy metal content. Measurements on heavy metal content in tailings soil and plant tissues was done using inductively coupled plasma optical emission spectroscopy. The differences between heavy metal concentrations found in plant tissues will indicate whether zeolite is an effective tool for heavy metal immobilization for mine reclamation.

2. Materials and Methods

Greenhouse and experiment set up

Materials:

1 L pots - 120
Plastic garden labels - 120
50 L totes - 3
25 L totes - 3
Whirl pack bags - 6
55% P_2O_5
Zeolite - 1 kg
pH meter - 1
Rubber gloves - 1 pair
Face mask - 1
Sharpie - 1

Three 50 L totes were filled with approximately 43 L of tailings and brought back to the greenhouse. To determine the total weight of tailings in each tote a pre-weighed 1 L pot was filled with tailings and weighed again; 1 L of our tailings weighed 1.235 kg. Therefore in each tote we had about 53 kg. A low concentration of zeolite to tailings ratio was found to be 5 g of zeolite per 1 kg of tailings. For the high zeolite concentration, we used 30 g of zeolite per 1 kg of tailings. Therefore 265.5 g of zeolite was added to one tote for the low concentration and 1593.0 g of zeolite was added to the second tote for our high concentration. The third tote was left as pure tailings. All totes were mixed separately for 10 minutes by hand while wearing long rubber gloves and a face mask. The mixing was done outside to ensure maximum ventilation as tailings dust can be toxic.

After mixing, 23 L of tailings was transferred separately from each tote into 3 smaller 25 L totes. Then we had two totes containing pure tailings, two with low zeolite concentration and two with high zeolite concentration. Multiple pH measurements were taken which ranged from 8.93 to 8.45. In the smaller totes the pH was adjusted by gradually adding aliquots of 250 mL of diluted 55% P_2O_5 solution. This solution was 9 parts deionized water to 1 part 55% P_2O_5. After each addition of the acidic solution the bins were hand mixed for 10 minutes while wearing gloves and a mask. Measurements of pH were taken after each mixing period until the pH was around 6.

In the end this gave us three totes of tailings - one with no added zeolite, a low zeolite concentration and a high concentration - at a basic pH and another three totes of differing zeolite concentrations at an acidic pH. For later analysis, soil samples of about 30 g were taken from each tote and put in labeled whirl pack bags placed in. The six sample bags were placed in a freezer. Then, 20 1 L pots were filled with acidic tailings containing no zeolite, another 20 pots were filled with acidic tailings with a low concentration of zeolite and finally 20 more pots were filled with acidic tailings which had a high zeolite concentration. The same was done for tailings with a basic pH. Bluebunch wheatgrass seeds were sown into half of the pots and field locoweed seeds were sown into the remaining half. Bluebunch seeds do not need prior preparation before planting, however field locoweed seeds do. A day ahead of planting, the field locoweed seeds were scarified by shaking them in a jar with coarse sandpaper lining the inside. The jar was shaken for a good two minutes and then the seeds were soaked in water for 24 hours. This scarification and soaking process promotes maximum germination for the field locoweed. Around 50 bluebunch seeds were planted per pot and 100 field locoweed seeds were planted in the other pots. This gave us a replication of 10 pots for each seed type per treatment which were assigned with numbers from 1 to 12. Each pot was labeled with a number on the plastic garden markers according to its treatment and seed type. The pots were placed on the tables in the greenhouse according to a random block design generated by excel (see figure 1).

The plants grew in the greenhouse for about three months from June 18th to August 28th. During the first week the pots were watered every day with around 50 to 100 mL of hose water. In the following weeks the pots were watered every other day. After the first month of growing the pots were watered three times a week.

Harvesting plants and preparing for analysis

Materials:

2000 mL tupperware - 1
Metal stir rod - 1
Paper towel - 3 rolls
Small paper bags (dimensions 25 x 18 x 8 cm) - 138
Small plastic bags (dimensions 5 x 8 cm) - 120
15 L bucket - 12
2 mm sieve - 1
Rubber gloves - 1 pair
Face mask - 1
Sharpie - 1
Analytical Fisher Scale - 1
Oven - 1
Laboratory gloves
Mortar and pestle - 1
70% Ethanol
Scissors - 1

Each paper bag was labeled according to the treatment types and plants in the pots. After labeling, the bags were all pre-weighed and the weight was recorded. Then, the plants were harvested. For the easiest extraction of the plant from the pot, the tailings had to be dry and the soil loosened with a metal stir rod. After each use of the metal rod it was cleaned with paper towel. Each plant was then gently hand-picked just below the root base to make sure as much of the roots as possible were harvested with the plant. Then each plant was rinsed for a few minutes in a 2000 mL Tupperware which was half filled with clean water. The water was changed out every five to six rinses to ensure there was minimal cross contamination between plant samples. The rinsed and harvested plant was padded with paper towel and placed on its respective paper bag to dry for 2 to 3 hours. Then the plant and the bag were weighed together and the weight was recorded. After weighing, the plants in bags were put in the oven set at 65°C for 48 hours. Two days later the dried plants in their bags were removed from the oven and weighed again. This weight was recorded and used to calculate the dried biomass of each plant. To keep the plants dry for the next step the bags were placed in a drying cabinet.

Once all the plants had been harvested the remaining tailings in the 1 L pots were combined according to their treatment. Each pot with acidic tailings with no added zeolite was combined in 15 L bucket and so on. In the end there were 12 buckets containing the unique treatments of field locoweed or bluebunch grass in acidic or basic tailings with high, low or no zeolite added. The buckets were hand mixed for five minutes while wearing rubber gloves and a face mask. Then 30 g samples were taken from each bucket transferred to labeled paper bags and oven dried. Along with these post plant growth samples, 15 g of tailings from samples placed in the freezer before growth put in labeled paper bags. All soil samples were oven dried at 60 °C for 48 hours. The dried tailings samples were then sieved and put in labeled plastic bags to be sent to the Analytical Lab in Victoria for heavy metal analysis using ICP-OES.

To prepare the plant samples for major elements analysis using ICP-OES they have to be ground to a fine powder. Because each dried plant had such a low biomass the mortar and pestle was the best option to make sure as little as possible of the sample was lost during the grinding process. Each plant was ground in a mortar and transferred to a pre-labeled plastic bag. For the larger plants it was helpful to cut them up into smaller pieces with scissors before grinding. Between grinding each plant sample the mortar and pestle was cleaned with 70% ethanol and dried with paper towel. This process was very time consuming, overall taking two weeks. Once complete, the plant samples were sent to the Analytical laboratory in Victoria for analysis.

Results

Due to the backlog of samples sent to the Analytical laboratory in Victoria, the heavy metal analysis on plant tissue and tailings soil has been delayed past this experiments projected timeline. Data was collected on dry plant biomass and this was statistically analyzed using ANOVA in minitab18. There were no significant differences in bluebunch wheatgrass dry biomass between treatments, however there was a statistically significant difference found in the field locoweed biomass (see figures 1 and 2). The analysis of variance using a significance level of 0.05 showed a p-value of 0.522 for bluebunch wheatgrass mean weights, therefore the null-hypothesis of no variance between means could not be rejected. In the analysis of variance done with field locoweed mean weights the p-value was 0; therefore the null-hypothesis was rejected and there was a statistically significant difference found among means. This difference was most likely due to the change in tailings pH. For the field locoweed, a more acidic tailings was correlated with a lower mean biomass. This effect was not noted in bluebunch wheatgrass. However, it is interesting to note that the added zeolite seemed to be related to lower mean

weight in bluebunch samples. In contrast, the zeolite added to field locoweed seemed to be related to higher biomass, although these results were not significant.

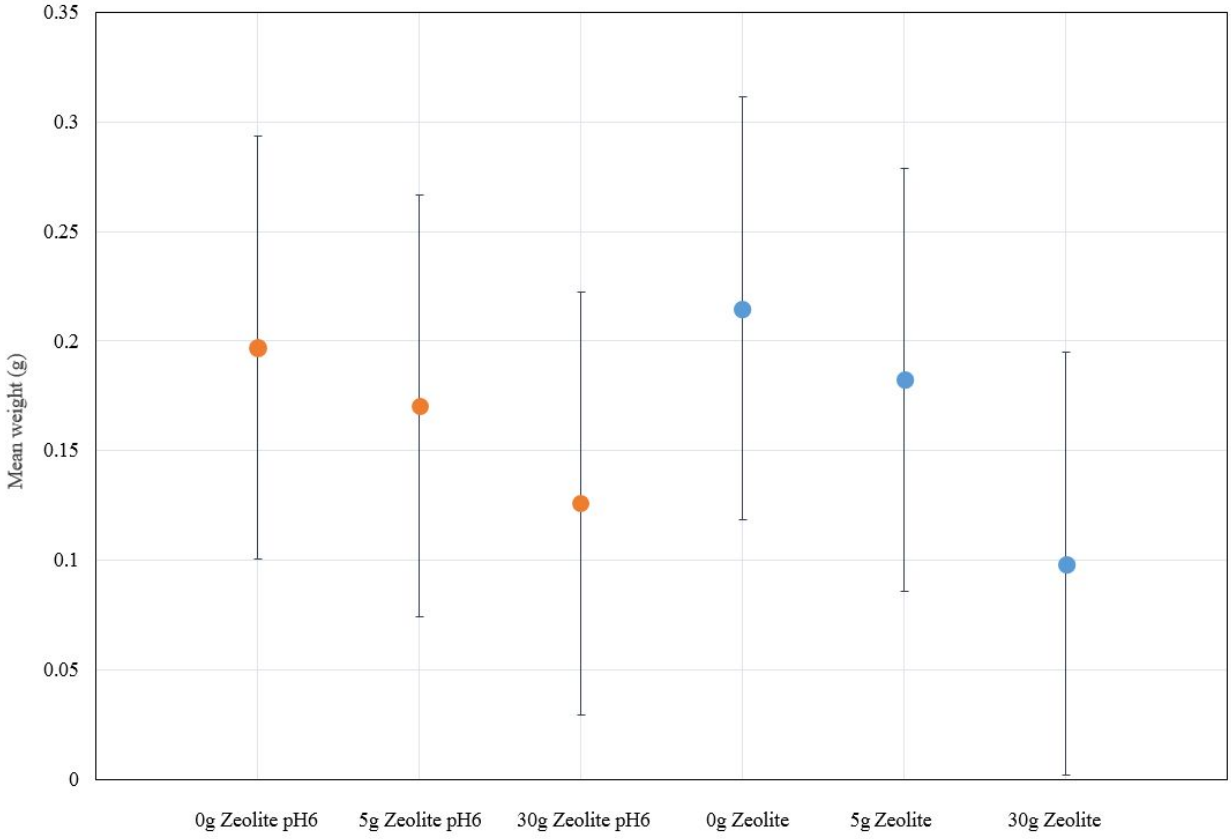

Figure 1. Bluebunch wheatgrass mean dry weight according to treatment type (n=10). Bars outline 95% Confidence interval. Analysis of variance p-value 0.522.

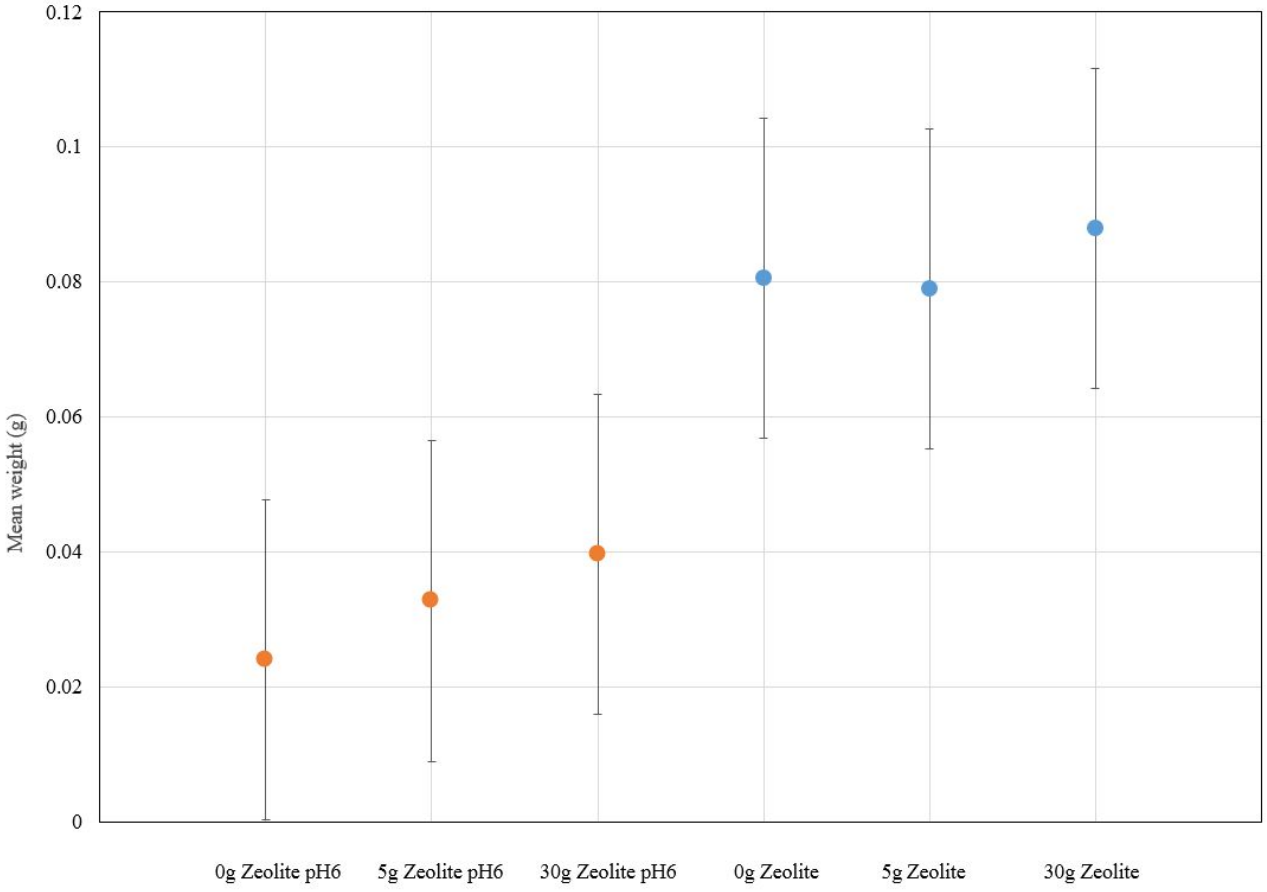

Figure 2. Field locoweed mean dry weight according to treatment type (n=10). Bars outline 95% Confidence interval. Analysis of variance p-value 0.

Discussion

Although the differences in recorded plant biomass weight seem to be more strongly correlated to changes in tailings pH, the results indicate there may be alternate effects of zeolite on plant growth depending on the plant species. Field locoweed is a nitrogen fixing plant, and therefore does not rely on the presence of usable forms of nitrogen, nitrate and ammonium, in the soil. Zeolites cation adsorbing capabilities enable it to adsorb heavy metals in the soil as well as the positively charged ammonium. For plants that rely on the presence of ammonium such as bluebunch wheatgrass, this could inhibit growth and explain the results seen in figure 1. For field locoweed however, the plant does not rely on the presence of ammonium and would not hinder the plants growth. The results indicate that zeolite may improve field locoweed growth. This could be due to the zeolite inhibiting heavy metal uptake into the plants tissues, although it is difficult to tell without the results from the plant tissue heavy metal analysis.

Soil acidity and alkalinity also played a large part in plant growth. Both species of plants on average did better in alkaline tailings. Field locoweed showed the most dramatic difference between the two pH treatments. Bluebunch wheatgrass was more tolerant of acidic tailings soil. Bluebunch wheatgrass is found in the interior grasslands of BC where the soil pH is around 6.3 therefore it's possible that the bluebunch tolerated acidic tailings because it had a similar pH to the soil it usually grows in.

Further research is required to determine the effects of zeolite on plant growth in mine tailings. Plant tissue heavy metal analysis could offer more statistically significant data on zeolites effects. In the future, in order to eliminate the variable of pH on plant growth, pH should not be altered in mine tailings. A study focusing on a single plant species and its growth in mine tailings with added zeolite would help to determine the viability of zeolite as a mine amendment tool. The current use of zeolite in water treatment and industrial settings is a promising indicator of the ability zeolite could have in mine tailings treatments.

References

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Appendix:

Table 1. Bluebunch wheatgrass

Treatment	Mean Weight (n=10)	StDev	95% CI
0g Zeolite pH6	0.197	0.1375	(0.1004, 0.2935)
5g Zeolite pH6	0.1704	0.1218	(0.0739, 0.2669)
30g Zeolite pH6	0.1259	0.1163	(0.0294, 0.2224)
0g Zeolite	0.215	0.234	(0.1185, 0.3115)
5g Zeolite	0.1822	0.1518	(0.0857, 0.2787)
30g Zeolite	0.0982	0.1182	(0.0017, 0.1947)

Table 2. Field locoweed

Treatment	Mean Weight (n=10)	StDev	95% CI
0g Zeolite pH6	0.02404	0.01884	(0.00031, 0.04776)
5g Zeolite pH6	0.03273	0.02845	(0.00900, 0.05645)
30g Zeolite pH6	0.0397	0.02955	(0.01597, 0.06342)
0g Zeolite	0.0806	0.0367	(0.0569, 0.1043)
5g Zeolite	0.079	0.0529	(0.0552, 0.1027)
30g Zeolite	0.0879	0.0471	(0.0642, 0.1116)

Pod Doors

10	1	9	12
3	2	11	5
8	7	6	4

10	9	2	1
4	7	11	12
8	6	3	5

11	5	9	6
12	7	4	2
3	1	8	10

Wall

12	8	4	2
6	3	1	9
10	11	7	5

5	12	4	7
3	10	8	9
6	1	11	2

10	3	1	12
6	4	8	5
7	11	2	9

2	1	10	6
5	9	4	11
12	7	3	8

5	7	1	9
12	10	4	8
3	2	11	6

8	4	7	6
1	5	12	11
3	10	9	2

9	12	7	5
3	4	2	8
1	10	6	11

Windows

Legend

1 0 FL
2 0 B
3 0 FL Ph6
4 0 B Ph6
5 5 FL
6 5 B
7 5 FL Ph6
8 5 B PH 6
9 30 FL
10 30 B
11 30 FL PH 6
12 30 B PH 6

Figure 3. Outline of random block design used in greenhouse

Figure 4. Greenhouse set up.

Figure 5. Bluebunch wheatgrass (right) and field locoweed (left) before harvesting.