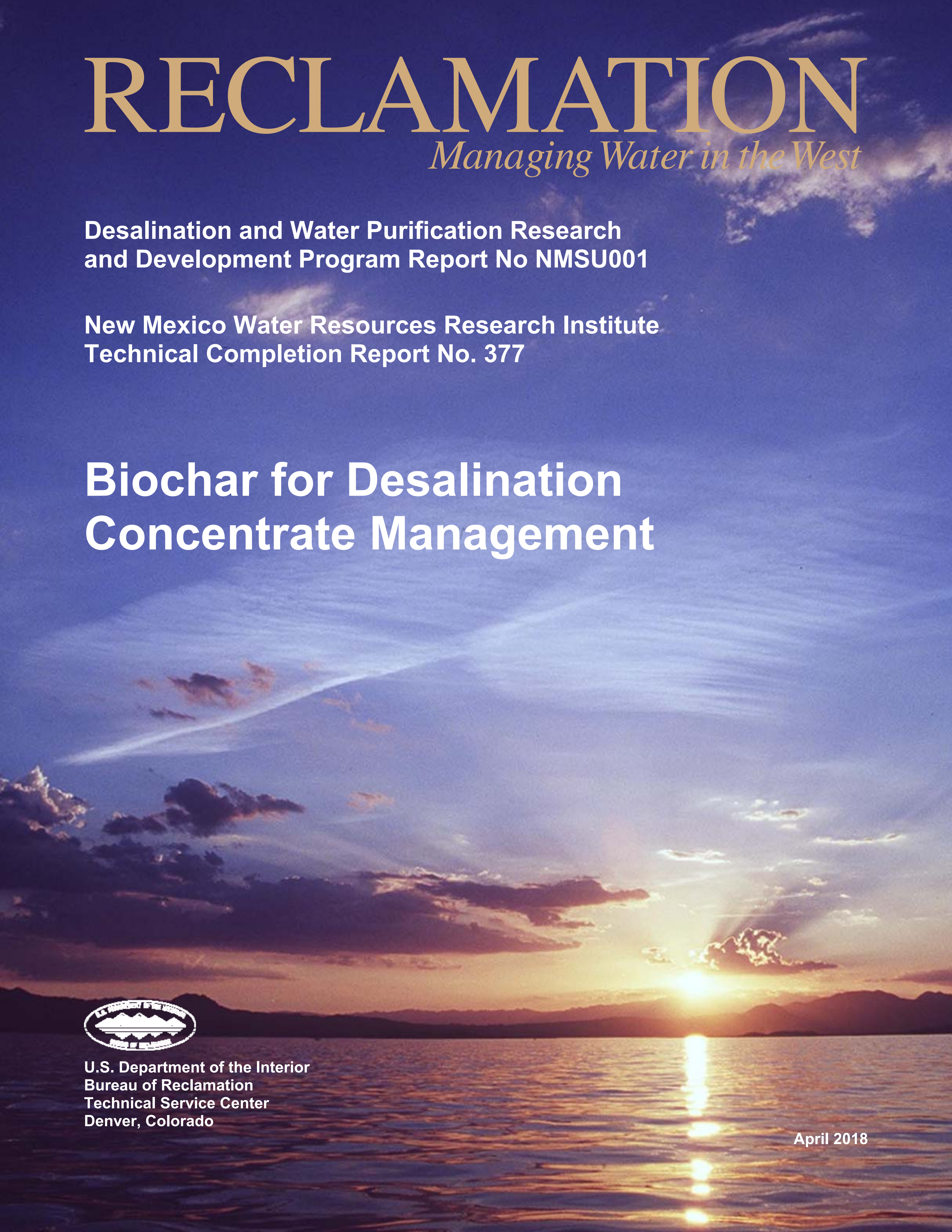

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Managing Water in the West

Desalination and Water Purification Research and Development Program Report No NMSU001

New Mexico Water Resources Research Institute Technical Completion Report No. 377

Biochar for Desalination Concentrate Management

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14. ABSTRACT
Results from this research on two species of *Atriplex*, halophyte forage shrubs native to the southwestern USA, show that salts taken up in the biomass are concentrated into the biochars during pyrolysis, and that pyrolysis conditions affect the amount of salt that can be leached with water. Increasing pyrolysis temperature increases the retention of calcium and magnesium ions but gives less consistent trends for the retention of potassium and sodium. The retention of some salt in the short-term suggests that, with more understanding of the salt formation and retention mechanisms, and optimization of the system, higher amounts of salt could be sequestered longer, while taking advantage of the carbon sequestration and soil quality improvement benefits associated with biochars.

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Biochar for Desalination Concentrate Management

Prepared for the Bureau of Reclamation Under Agreement No. R16AC0002

by

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New Mexico State University

Mission Statements

The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

Disclaimer

Acknowledgments

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Abstract

Disposal of concentrate from brackish water desalination is limited by concerns that salt may leach into freshwater sources. Prevention of salt leaching can greatly increase desalination concentrate management costs, and there are few options to recover those costs. One cost-recovery option for desalination concentrate disposal is using the concentrate as irrigation water for producing halophyte biomass for forage and for other applications. The purpose of this project is to determine how much salt is contained in halophyte biomass and how much salt will leach from biochars made from halophyte biomass. Results from this research will be useful for those managing high-salinity biomass streams, such as halophyte crop residues and animal manures. The ability to sequester salt in biochar (charcoal derived from the pyrolysis of biomass used as a soil amendment) would decrease the negative impacts from land-applications of high-salinity materials, including those used in desalination concentrate management systems.

Results from this research on two species of *Atriplex*, halophyte forage shrubs native to the southwestern USA, show that salts taken up in the biomass are concentrated into the biochars during pyrolysis, and that pyrolysis conditions affect the amount of salt that can be leached with water. Increasing pyrolysis temperature increases the retention of calcium and magnesium ions but gives less consistent trends for the retention of potassium and sodium. The retention of some salt in the short-term suggests that, with more understanding of the salt formation and retention mechanisms, and optimization of the system, higher amounts of salt could be sequestered longer, while taking advantage of the carbon sequestration and soil quality improvement benefits associated with biochars.

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INTRODUCTION

In New Mexico (USA), approximately 75 percent of groundwater is too saline for most uses without desalination (Reynolds 1962). Widespread implementation of desalination technologies is limited at inland locations since there are few options for disposing of the high salinity concentrate; options that are available, such as deep-well injection and pond evaporation, are difficult and costly. New options are needed that enable productive and local use of desalination concentrate, and that protect the soil and groundwater from salt contamination.

Halophytes are one option being explored by researchers as a way to use desalination concentrate to produce revenue. Halophytes, which include several thousand species of marine plants, grasses, shrubs, and trees, are plants that grow naturally in saline habitats in many different ecosystems, from coastal areas to mountains and lowland deserts (Glenn and Brown 1999). Halophytes have many productive applications: rehabilitating degraded lands, combating desertification, providing firewood and timber, creating shade and shelter, producing industrial crops and animal fodder, etc. If cultivated instead of conventional crops, halophytes can reduce fresh water use in agriculture since they can be irrigated with brackish water, if they need to be irrigated at all. Halophytes can be grown in soils too salty for normal crops and pastures, and thus, can make a significant contribution to human food security and desalination concentrate use (Glenn and Brown 1999, Soliz et al. 2011).

Biochar, charcoal produced from pyrolysis of biomass under moderate temperatures (~350-600 °C) and used as a soil amendment, may also play a role in sustainable desalination concentrate management systems. Biochar application has been shown by different studies to have a significant impact on several soil quality parameters (Barrow 2012), including: increasing soil capacity to sorb plant nutrients (Liang et al. 2006); increasing retention of plant-available water (Karhu et al. 2011); and increasing crop yields (Kimetu et al. 2008, Lehmann and Joseph 2015). Biochar application rates in the literature range from <1 Mg/ha to >150 Mg/ha, with a wide variety of application methods, and there is no consensus on an upper application rate limit. The few application rate limitations suggested are based on biochar ash content, as ash usually raises soil pH and salinity. During thermochemical processing, biomass components are distributed among the solid, liquid, and gas products. The biomass mineral matter (ash) is almost completely partitioned into the char fraction. Some of the salts undergo dehydration, oxidation or reduction reactions, but, in general, all elements besides C, H, N, and O in the biomass can be found after pyrolysis in the biochar (Gaskin et al. 2008). Past research has shown that at least some of the salt found in biochars can be dissolved and leached out by water (Brewer et al. 2011, Deal et al. 2012, Artiola, Rasmussen, and Freitas 2012, Wu et al. 2011). However, even if some of the salt can be leached out of biochar with sufficient washing (a function of salt solubility), to the best of our knowledge, no one has measured whether salt can purposefully be sequestered in biochar. The possibilities offered by sequestering salt from desalination concentrate in a solid, mineral form, in addition to soil quality improvements provided by biochar, are intriguing for addressing concentrate management challenges.

If growing halophytes on desalination concentrate and pyrolyzing halophyte biomass can sequester salt in biochar, it may be possible for farmers to manage concentrate on their own farms. Part of the farm could be dedicated to growing halophytes, such as *Atriplex*, a genus of forage crops suitable for arid regions like New Mexico (Glenn et al. 2013). Harvested biomass could be used for revenue generation, for example, sold as animal feed, or used as feedstock for pyrolysis to provide thermal energy. Biochars from pyrolysis could be applied to the halophyte growth area. In this way, salt from the irrigation water could be contained in one (still productive) part of the farm.

Justification for Work Performed

Disposal of concentrate from brackish water desalination is limited by concerns of salt leaching into and contaminating surface and ground waters. Measures to prevent leaching add substantially to concentrate disposal costs, with little or no opportunity to recover those costs. One option being explored is the use of concentrate as irrigation water for producing halophyte biomass for forage and other applications. Continued development of this option requires more knowledge of what happens to the salt in the concentrate after it is applied as irrigation water. The purpose of this project was to determine how much of the salt taken up by halophyte crops can be protected from leaching by pyrolysis of the biomass, that is, to determine the potential of sequestering salt in biochar. Results from this research will be useful for managing high-salinity biomass streams, such as halophyte crop wastes and animal manures, and for evaluating local concentrate disposal options involving biomass with a potential for producing economic and/or environmental returns. The ability to sequester salt in biochar would decrease the negative impacts of applying high-salinity materials to land, including those materials used in desalination concentrate management systems.

Results from this project will serve as preliminary data for the development of salt balances and future mechanistic studies for salt storage, transport, and sequestration. The goal of such studies would be to understand and to quantify how land-applied salt within concentrate moves within the soil-plant interface, and, therefore, to evaluate the potential environmental impact of desalination concentrate utilization for field crop and biochar production.

PROJECT OBJECTIVES

Project Objectives

The specific objectives of this project were to:

- Determine the quantity and composition of salt in *Atriplex* biomass grown on concentrate.
- Determine the quantity, composition, and leachability of salt in *Atriplex*-derived biochars.
- Submit follow-on funding proposals to study salt sequestration mechanisms and the potential of integrated water desalination-biomass growth-pyrolysis systems for managing salt while producing thermal energy.

Degree of Project Objective Completion

The project objectives were completed. Two species of *Atriplex* grown on concentrate were characterized for biomass salt content including the differences between stem and leaf biomass fractions. Five biochars were made for each species under different conditions and those biochars were leached to quantify retention of major salt cations (metal ions). One proposal was submitted and the project completed for a National Science Foundation (NSF) Innovation Corps grant to evaluate the commercial potential for a brackish water desalination system powered by biomass energy. Another proposal, a revised CAREER proposal, was submitted to the NSF to study salt immobilization mechanisms; that proposal included this preliminary data and is under review.

METHODS

Sample Preparation and Collection

In September 2014, researchers from the University of Arizona, Texas A&M University – Kingsville, and New Mexico State University planted two halophyte crops, *Atriplex canescens* and *Atriplex lentiformis,* on a one-acre (0.4 ha) plot at the Brackish Groundwater National Desalination Research Facility (BGNDRF), Alamogordo, NM. These shrubs were irrigated with reverse osmosis (RO) concentrate and a blend of brackish water from two wells with total dissolved solids (TDS) concentrations of 4,063 ppm and approximately 3,450 ppm, respectively (Gallaher et al. 2015). On May 16 and 17, 2016, the shrubs were harvested and partially dried in the open air. On May 18, 2016, the biomass was cut into pieces (~10-30 cm long) and transported to the Leyendecker Plant Science Center, Las Cruces, NM. Harvested biomass was then cut into smaller pieces (2-5 cm long) using hand pruners, and dried using a gas convection oven (Stone Conveyor Co., Inc.) at 100°C for two days prior to storage to prevent mold.

Biochar Production

Slow pyrolysis in a custom-built batch slow pyrolyzer was used to prepare biochars from *A. canescens* and *A. lentiformis*. The pyrolyzer consists of a single-zone horizontal tube furnace (model GHA 12/450, Carbolite, Hope Valley, UK) with an 18-inch (46 cm) heating zone sized to fit a 5.5-inch (14 cm) O.D. 304 stainless steel reaction tube with a 0.25 inch (6 mm) wall thickness. Two circular 303 stainless steel plates with large holes were secured inside the reaction tube with screws. Wire cloths (304 SS, 40-mesh) were placed between the plates on the halophyte biomass side to contain the biomass particles while allowing for gas flow. The reaction tube had end-caps secured with high temperature glass-mica ceramic O-rings held in place by clamps. The inlet end-cap had two openings, one for a thermocouple (Super OMEGACLAD XL, Omega Engineering Inc., Stamford, CT, USA), and the other for a nitrogen gas inlet. The thermocouple was connected to a portable handheld data logger (OM-EL-ENVIROPAD-TC, Omega Engineering Inc., Stamford, CT, USA) to record the temperature of the biomass undergoing pyrolysis at 5 min intervals. The exit end-cap had a 0.95 cm O.D. tube maintained at a temperature of 300°C by a heat tape (XtremeFLEX BWH, BriskHeat Corp, Columbus, OH, USA) with a temperature controller (SDC Digital Benchtop, BriskHeat Corp., Columbus, OH, USA). The tube fitted to the exit end-cap was connected to a condenser consisting of a large glass Erlenmeyer flask set containing roughly 700 ml of water placed in an ice bath. The pyrolysis vapors bubbled through the condensation setup to capture the bio-oil (Zhang, Idowu, and Brewer 2016).

Halophyte biomass (300-500 g) was loaded into the reaction tube between the perforated steel plates. An inert environment was maintained by flowing nitrogen gas at a rate of 1 L min^{-1} through the reaction tube. The furnace was heated to the set temperature (400, 500 or 600 °C) at a rate of 5 °C min^{-1} with a dwell time of 60 min. After the reaction, the pyrolyzer was allowed to cool overnight under nitrogen. (An inert atmosphere and an external electrical heater were used here to enable better reaction condition control, to increase repeatability, and to increase laboratory safety; most commercial-scale pyrolysis systems would use partial internal combustion to provide heat in a limited-oxygen environment. The choice of an inert environment was expected to have a negligible effect on the cation retention in the biochar. This assumption will be tested in the future once a partial combustion pyrolysis reactor with good control is available for the laboratory.) Once cooled, the reactor was disassembled, and the biochar removed, weighed, and stored in sealed containers. The weight of the water condenser was measured before and after pyrolysis to estimate bio-oil yields. The oils that condensed inside the reaction and exit tubes were not quantified. The yield of biochar was estimated by dividing the biochar weight by the feedstock weight on a dry basis. For cleaning, parts were rinsed with methanol, then placed in the furnace at 600 °C for 60 min to burn off tar residues.

Salt Leaching and Soluble Ion Analysis

The biochar was crushed with a ceramic mortar and pestle, and sieved to particle sizes between 10 mesh (2.0 mm) and 60 mesh (0.25 mm) to represent the size of crushed biochar that might be applied to a field and to narrow the size range of the particles creating the flow conditions. A constant head permeameter (Test Mark Industries, USA), consisting of a 6.03-inch (15.3 cm) long clamping ring acrylic chamber with an I.D of 2.5 inches (6.4 cm), was used for the leaching studies. The chamber had two anodized aluminum end-caps and three anodized clamping rings.

A cylindrical insert was made from a clear polypropylene machined to a length of 6 inches (15.2 cm), O.D. of 2.5 inches (6.4 cm) and I.D of 0.75 inches (1.9 cm) to reduce the size of the sample chamber. The apparatus had an inlet valve on the top end-cap and an outlet valve below. Porous stones placed below and above the permeameter prevented biochar from flowing into and clogging the valves. O-rings around the porous stones prevented leakage between the insert and the chamber walls. A plastic tube was connected from the inlet valve to a funnel clamped 1 m above the valve for feeding the water.

The cylindrical insert (~44 cc) was filled with the crushed biochar (biochar weights shown in Appendix Table A1) and the funnel was filled with deionized water. The outlet valve was opened slowly to allow the water to flow. Approximately 15 seconds was needed for the water to fill the sample chamber and to exit the outlet valve. During leaching, ten 20-ml aliquots of the leachates were collected in centrifuge tubes. The pH and electrical conductivity (EC) of the leachates were measured with a pH/Con 510 Benchtop Meter (Oakton Instruments). The leachates were then analyzed for alkali and alkaline earth metal (AAEM) cations using an Optima 4300 DV inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Inc. USA) using the EPA 200.7 ICP-OES method. The first three 20-ml aliquots of leachate were analyzed for corresponding anions produced by the dissociation of the alkali and alkaline earth metal salts using an ICS-2000 ion chromatography system (Dionex) using the Anion Quantification Method.

Biomass and Biochar Total Cation Analysis

Biomass samples included just leaves, just stems, and a mixture of leaves and stems in a 50/50 weight ratio. Halophyte biomass, unleached biochar, and leached biochar samples (0.2 g) were acid digested with 6 ml of 30% hydrochloric acid and 6 ml 70% nitric acid in a Multiwave 3000 Microwave Reaction System (Anton Paar). Solutions from the digested samples were analyzed using the ICP-OES to determine the AAEM cations present.

RESULTS AND DISCUSSION

Biomass Cations

Results from ICP-OES analysis of digested biomass samples showed that *A. lentiformis* biomass contained more salts than *A. canescens* biomass, with fractions of Na and K representing the differences between the two species (Table 1). K present in *A. canescens* and *A. lentiformis* ranged from 61-64% and 37-52% of the AAEM, respectively. *A. canescens* contained 1-13% Na of AAEM, while *A. lentiformis* contained 19-43% Na. The AAEM fraction of Ca and Mg ranged from 7 to 17% for both species. There were more salts in the leaves than in the stems for both species, which was expected due to how *Atriplex* spp. manage salinity by partitioning excess salts into bladders in their leaves (Panta et al. 2014, Flowers, Galal, and Bromham 2010).

TABLE 1.—AAEM in halophyte biomass components. Percents represent the concentration of that element relative to the total concentration of AAEM.

Biomass	Ca (mg/g)	Mg (mg/g)	K (mg/g)	Na (mg/g)	Sum (mg/g)	Ca (%)	Mg (%)	K (%)	Na (%)
A. canescens leaves	10.0	7.6	42.8	6.6	67.0	14.9	11.4	63.9	9.9
A. canescens stems	1.7	1.7	7.1	0.1	10.6	15.6	16.5	66.9	1.0
A. canescens leaves + stems (50/50 weight ratio)	6.0	4.3	24.4	5.2	40.0	15.1	10.8	61.2	13.0
A. lentiformis leaves	9.5	6.0	28.8	32.6	76.9	12.3	7.8	37.5	42.4
A. lentiformis stems	3.1	2.3	9.4	3.5	18.4	16.9	12.6	51.2	19.3
A. lentiformis leaves + stems (50/50 weight ratio)	6.8	4.5	19.8	21.9	52.9	12.8	8.4	37.5	41.3

Pyrolysis Yields

Biochar yields ranged from 30-39 wt.%; yield decreased with increases in temperature, with a greater decrease observed from 400 °C to 500 °C compared to 500 °C to 600 °C (Table 2). The produced biochars from both *A. canescens* and *A. lentiformis* were uniformly black in color with negligible odor, indicating complete carbonization and effective removal of volatiles from the pyrolysis reactor. Since cations are expected to simply concentrate in the biochar fraction as organic material is volatilized, the relative proportions of metal composition were expected to remain the same from the biomass to the biochar. Bio-oil yields ranged from 5-33%, and increased with increasing temperature for both *Atriplex* spp.

Table 2.—Biochar yields of halophyte biomass at different pyrolysis temperatures.

Feedstock	Pyrolysis temperature (°C)	Feedstock Mass (g)	Biochar yield (wt. %)
A. canescens	400	501	37.7
A. canescens	500	500	31.3
A. canescens leaves	500	300	33.6
A. canescens stems	500	300	34.3
A. canescens	600	300	30.3
A. lentiformis	400	500	39.6
A. lentiformis	500	300	31.8
A. lentiformis leaves	500	300	35.8
A. lentiformis stems	500	300	32.0
A. lentiformis	600	300	32.0

Biochar Leachate pH and Electrical Conductivity

The average flow rate of the biochar leachate after the chamber was filled was observed to be approximately 0.7 ml/s. Leachare pH values are shown in Figs. 1 and 2. For *A. lentiformis* biochar, the pH of the leachates remained relatively constant between 9 and 10, with a slight decrease in leachate pH with pyrolysis temperature (Fig. 1). Biochar made from the stem fraction had lower leachate pH than biochar made from the leaf fraction. For *A. canescens biochar*, leachate pH varied between approximately 7.5 and 11, with no change to a slight decrease in pH as leaching continued (Fig. 2). Leachate pH was lower for lower pyrolysis temperatures, and lower for stems than for leaves.

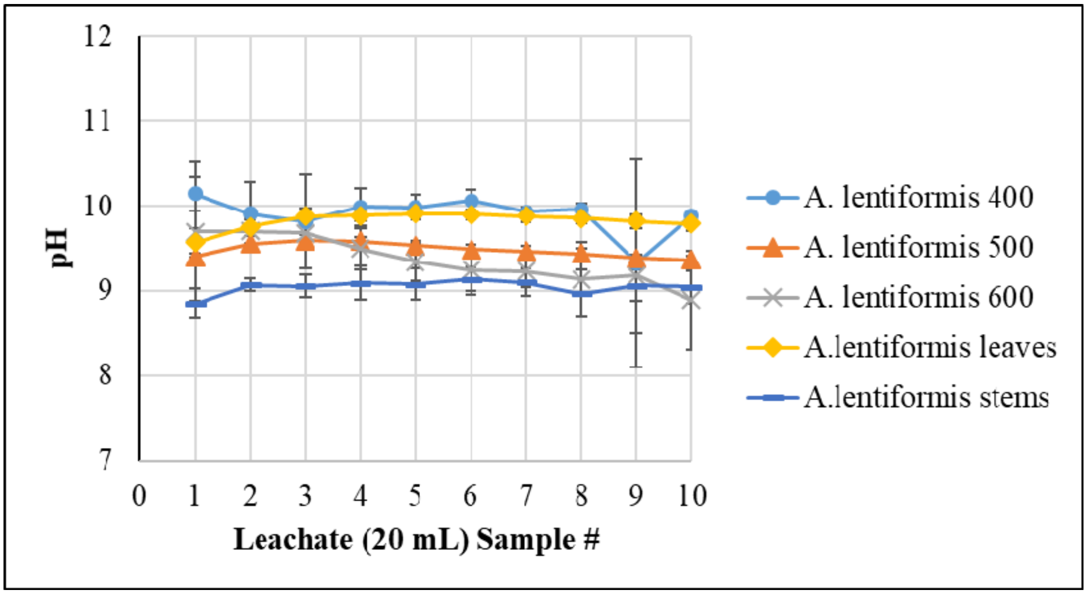

Figure 1.—Average pH of *A. lentiformis* biochar leachates at different pyrolysis temperatures (shown as numbers). Error bars indicate one standard deviation (n = 3).

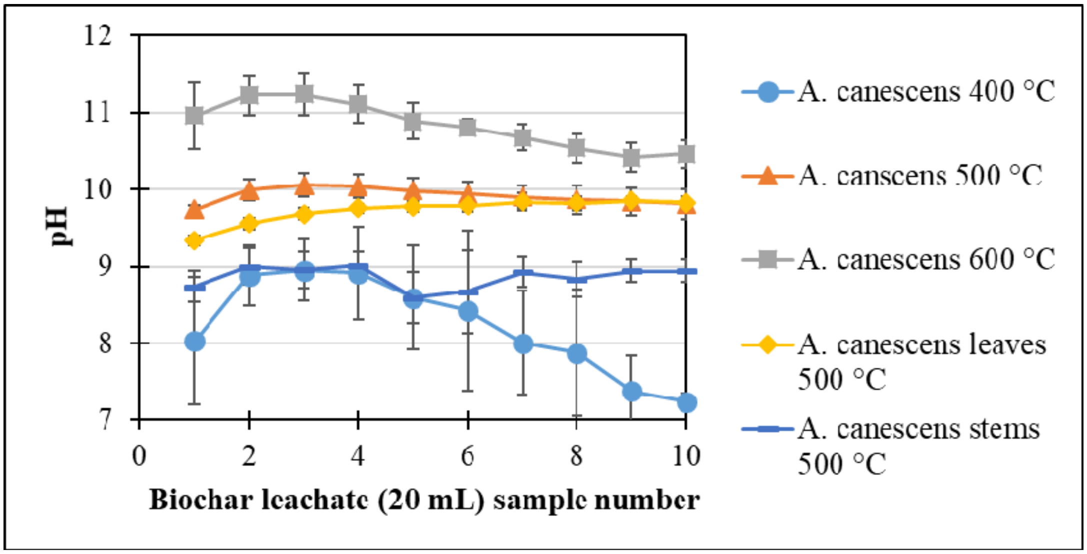

Figure 2.—Average pH of *A. canescens* biochar leachates at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

Electrical conductivity (EC) for the leachates are shown in Figs. 3 and 4. For *A. lentiformis* biochar, leachate EC decreased exponentially with increased leaching. EC was substantially higher for the 600 °C biochar than the biochars made at the lower temperatures. Biochar made from the leaves produced leachates with greater EC than biochar made from stems (Fig. 3). For *A. canescens* biochar, leachate EC decreased slightly with increased leaching. Biochar made at 500 and 600 °C and biochar made from the leaves produced leachates with greater EC than biochars made at a lower temperature or from stems.

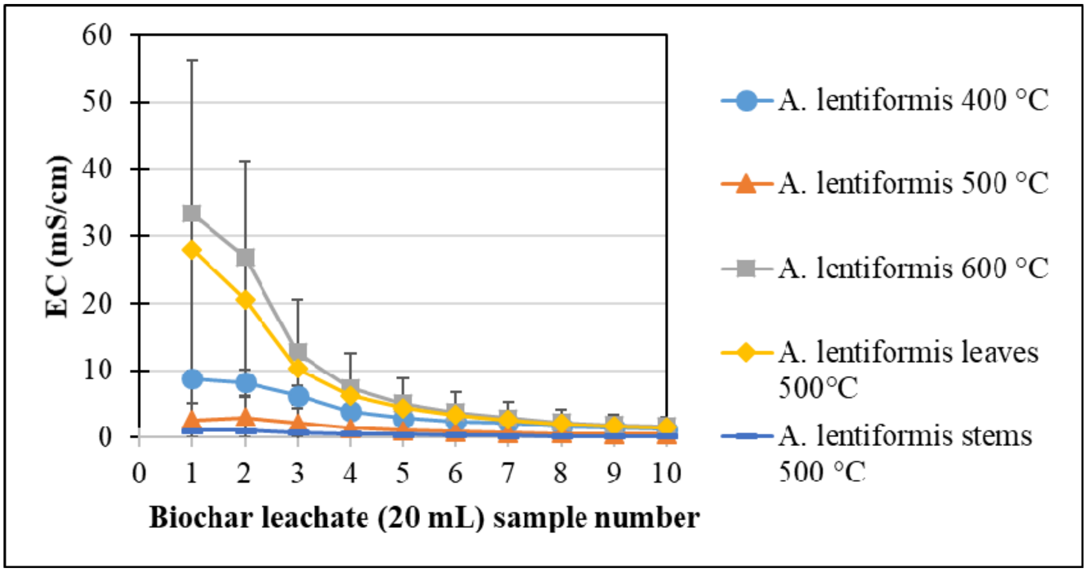

Figure 3.—Average electrical conductivity (EC) of *A. lentiformis* biochar leachates at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

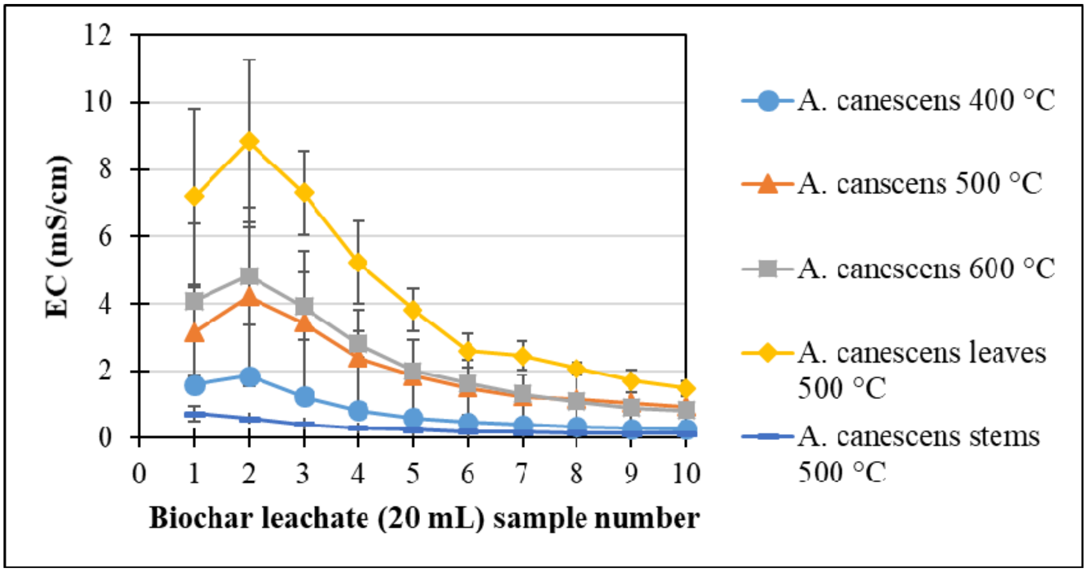

Figure 4.—Average electrical conductivity (EC) of *A. canescens biochar* leachate at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

Biochar Leachate AAEM Content

Calcium concentration for the biochar leachates are shown in Figs. 5 and 6. As expected from the total cation concentrations in the biochars and the lower solubility of Ca salts in water, the concentration of Ca in the leachate was approximately three orders of magnitude less than Na or K, i.e. mg/L compared to g/L. For both biochars, Ca concentration in the leachate was slightly higher for higher pyrolysis temperatures, and was higher for leaves than for stems. For the 400 °C biochars, almost no Ca was detected in the first few leachates, and concentration gradually increased with increased leaching.

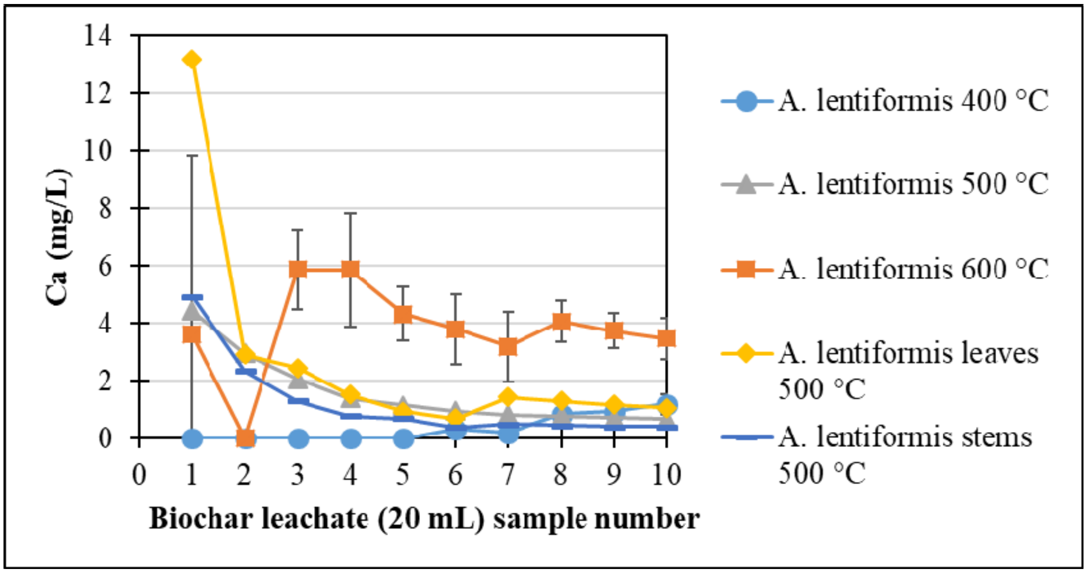

Figure 5.—Average Ca concentrations in *A. lentiformis* biochar leachates at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

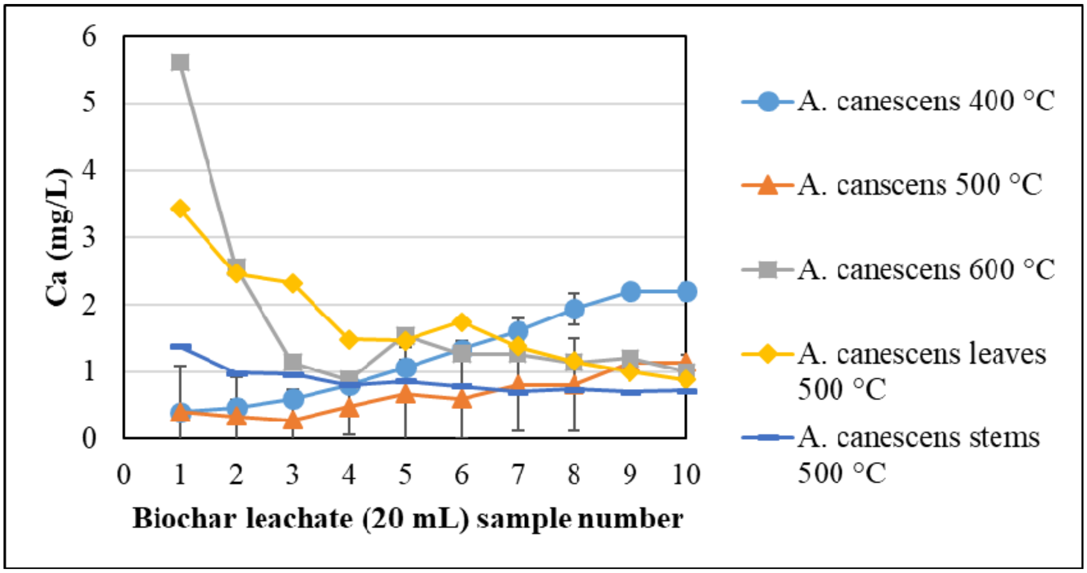

Figure 6.—Average Ca concentrations in *A. canescens* biochar leachates at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

Magnesium concentration for the biochar leachates are shown in Figs. 7 and 8. For both halophyte species, Mg concentration in the leachate was highest for the 400 °C biochars and about four times lower for the biochars made at the higher temperatures. Mg concentration decreased with leaching for the 400 °C biochars and remained relatively constant for other biochars. Concentrations for Mg were similar to or slightly higher than for Ca in the leachates.

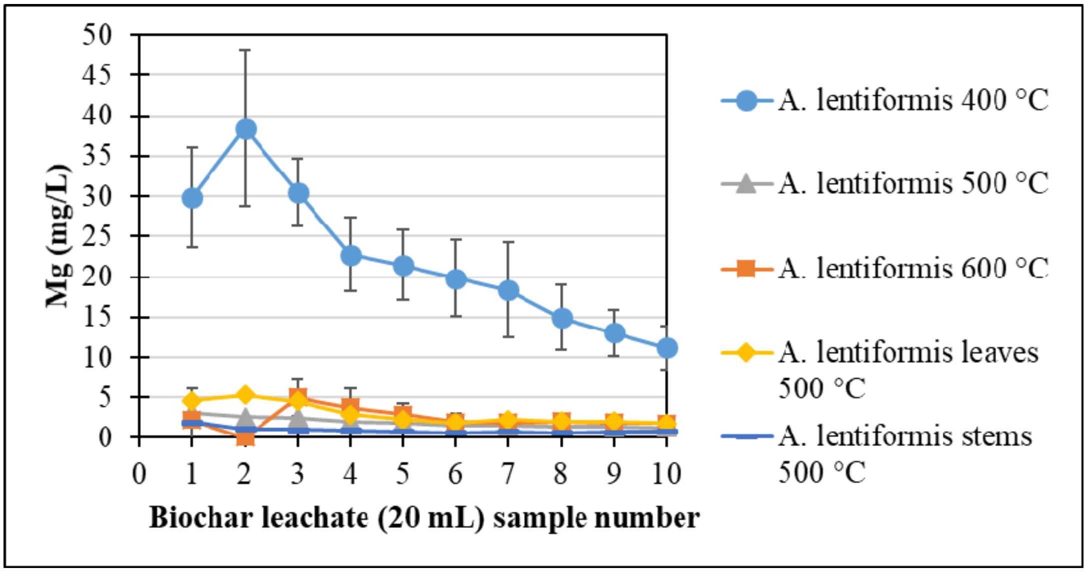

Figure 7.—Average Mg concentrations in *A. lentiformis* biochar leachates at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

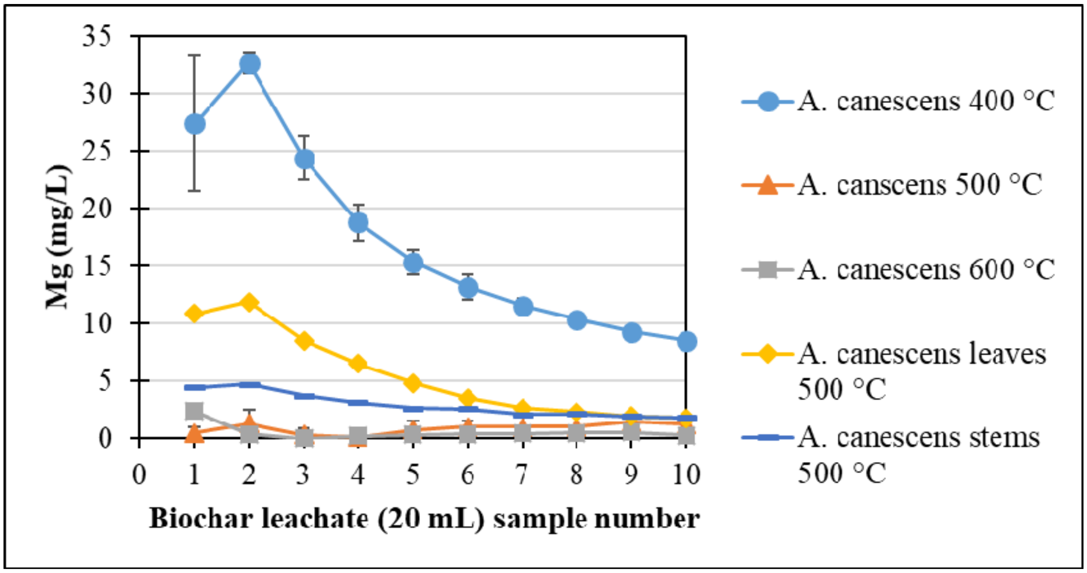

Figure 8.—Average Mg concentrations in *A. canescens* biochar leachates at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

Sodium concentration for the biochar leachates are shown in Figs. 9 and 10. For *A. lentiformis*, Na in the leachate was highest for the 600 °C biochar and decreased with pyrolysis temperature and with continued leaching. Na in *A. canescens* leachates was substantially lower than Na in *A. lentiformis* leachates, which reflects the lower Na concentration in the feedstock (Table 1).

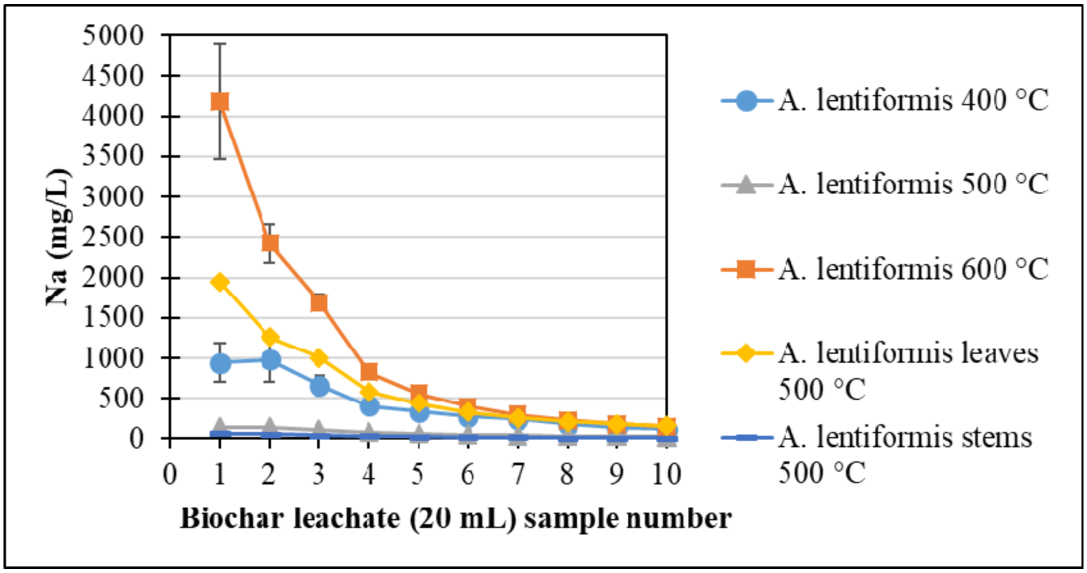

Figure 9.—Average Na concentrations in *A.lentiformis* biochar leachates at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

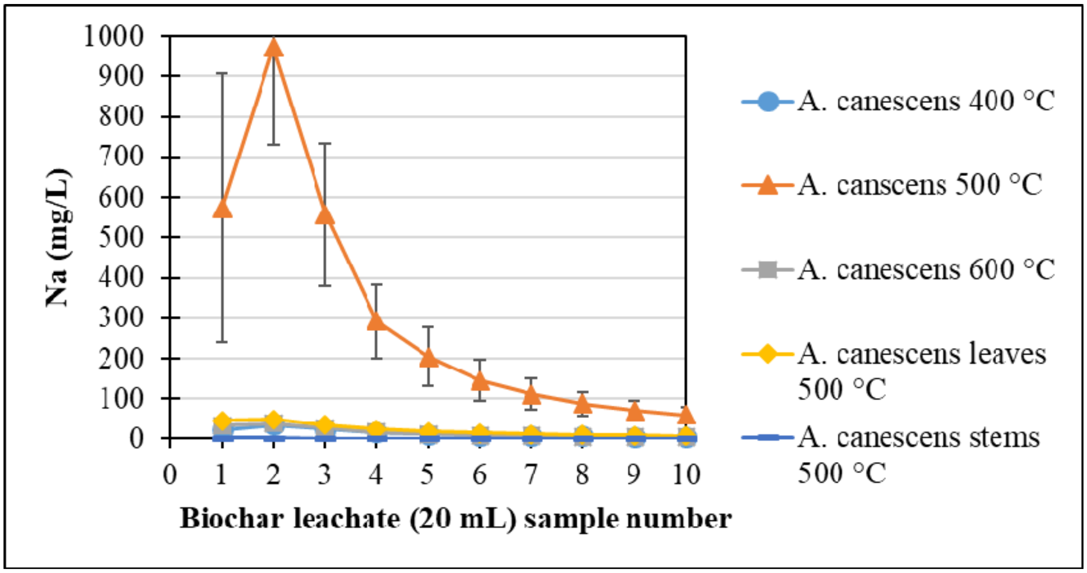

Figure 10.—Average Na concentrations in *A. canescens* biochar leachates at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

Potassium concentration for the biochar leachates are shown in Figs. 11 and 12. For both halophyte species, K in the leachate decreased with continued leaching and increased with pyrolysis temperature. K leachate content was higher for leaf biochars than for stem biochars.

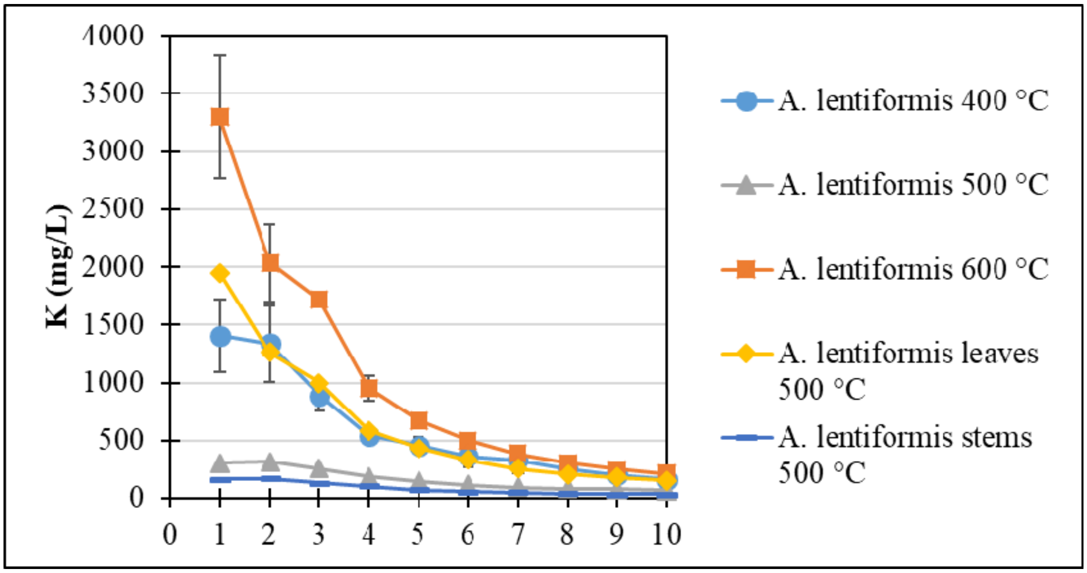

Figure 11.—Average K concentrations in *A. lentiformis* biochar leachates at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

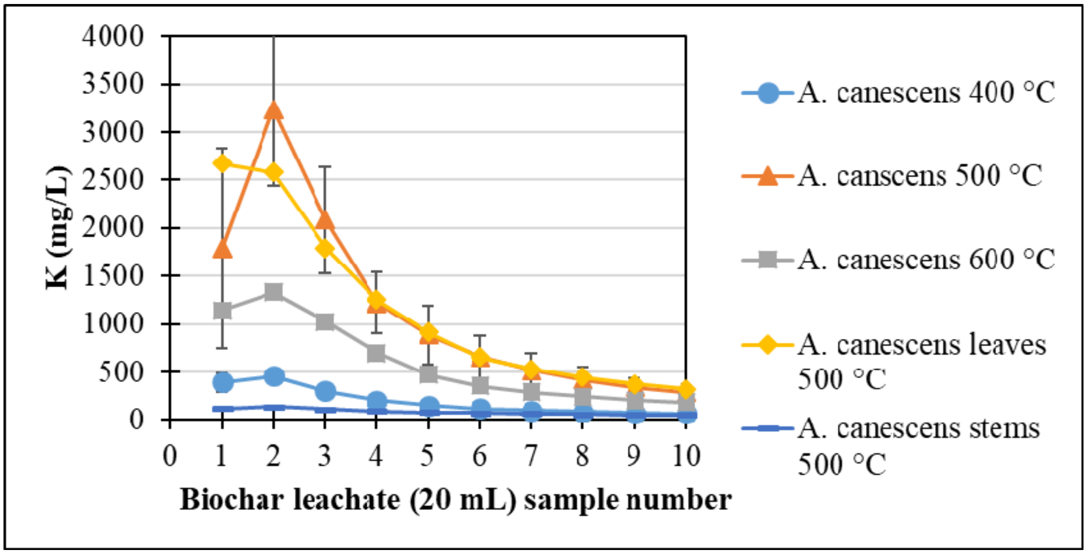

Figure 12.—Average K concentrations in *A. canescens* biochar leachates at different pyrolysis temperatures. Error bars indicate one standard deviation (n = 3).

Retention of AAEM Cations in Leached Biochars

The fraction of the AAEM retained in the halophyte biochar after leaching with five sample volumes of water varied with halophyte biomass and pyrolysis temperature (Figures 13-16, Tables A2 and A3). For Ca and Mg, biochars made at 600 °C retained more cations than biochars made at lower temperatures, and biochars made from the leaves retained more cations than biochars made from the stems (Figs. 13 and 14). Measured Ca retentions ranged from 36-100%; Mg retentions ranged from 50-104%. Notably, *A. canescens* biochars tended to retain a greater fraction of their Ca and Mg contents than *A. lentiformis* biochars, even though *A. lentiformis* biochars had 2-4 times higher concentrations of salt (Tables A2 and A3). This might be explained by the higher concentration gradients for the *A. lentiformis* biochars that would create relatively fast diffusion rates. For K, a plant macronutrient, retentions ranged from 35-73%, reflecting the greater solubility of K salts. *A. canescens* biochars had lower retention of K at 500 °C, regardless of biomass component, while retentions for *A. lentiformis* did not appear much affected by plant component or pyrolysis temperature (Fig. 15). Na retentions were low, ranging from 20-64%, except for *A. canescens* biochar made at 400 °C (85%) (Fig. 16). The generally lower retentions can be explained by the relatively high solubility of Na salts. The higher retention of Na in the lower temperature biochar warrants more investigation.

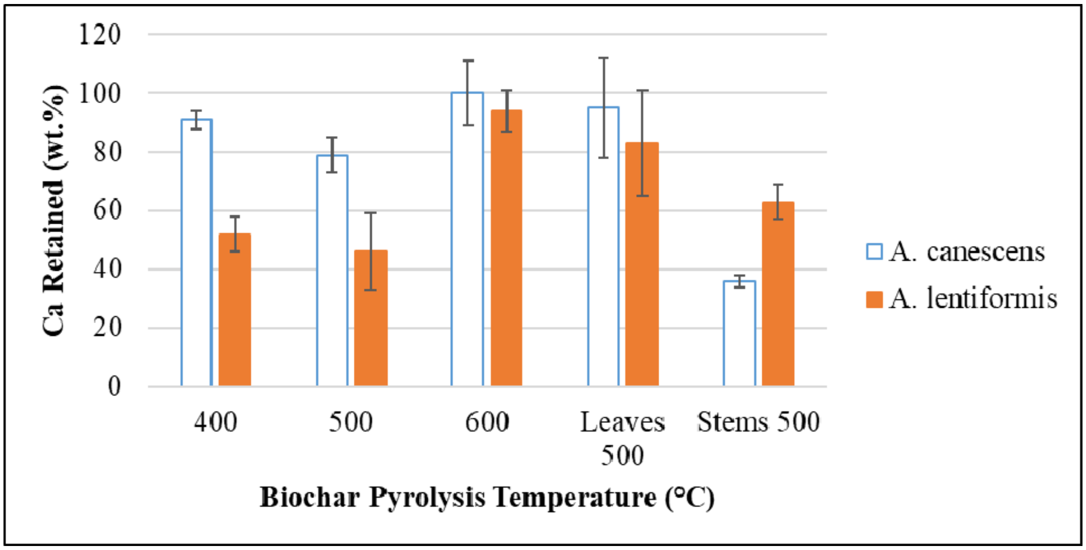

Figure 13.—Percent of calcium retained in biochars after leaching with 5 sample volumes of water. Error bars indicate one standard deviation (n = 3).

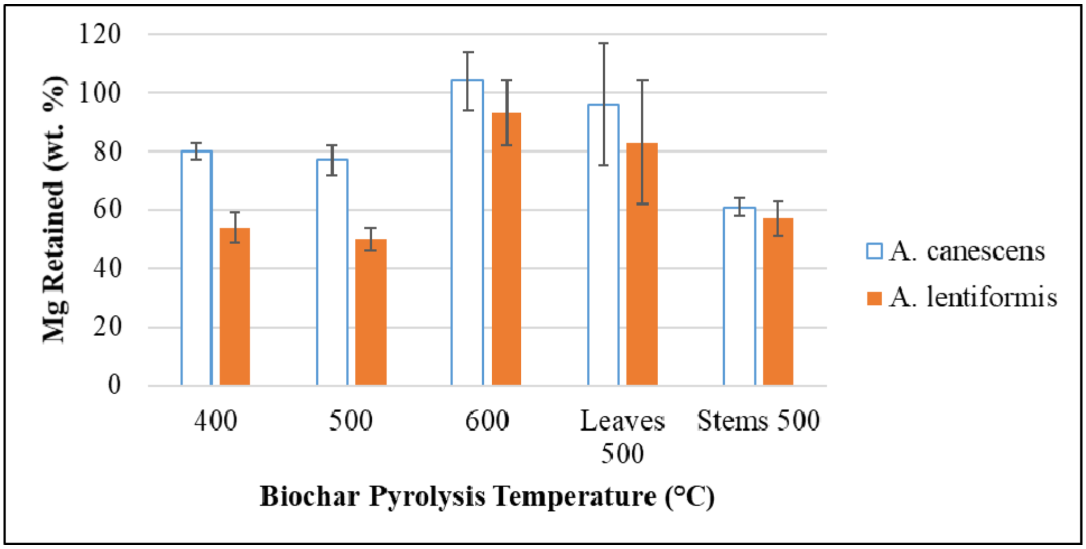

Figure 14.—Percent of magnesium retained in biochars after leaching with 5 sample volumes of water. Error bars indicate one standard deviation (n = 3).

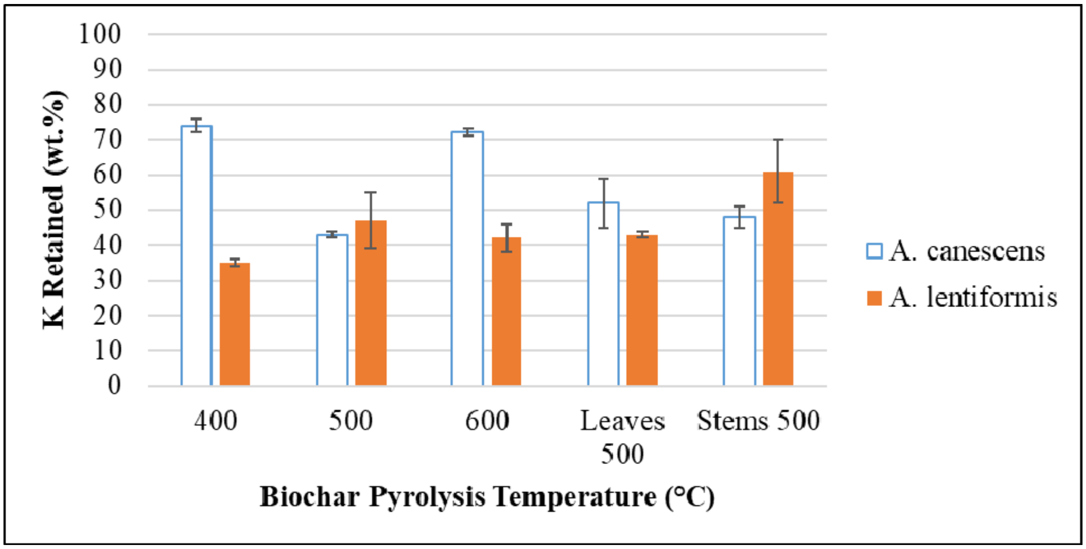

Figure 15.—Percent of potassium retained in biochars after leaching with 5 sample volumes of water. Error bars indicate one standard deviation (n = 3).

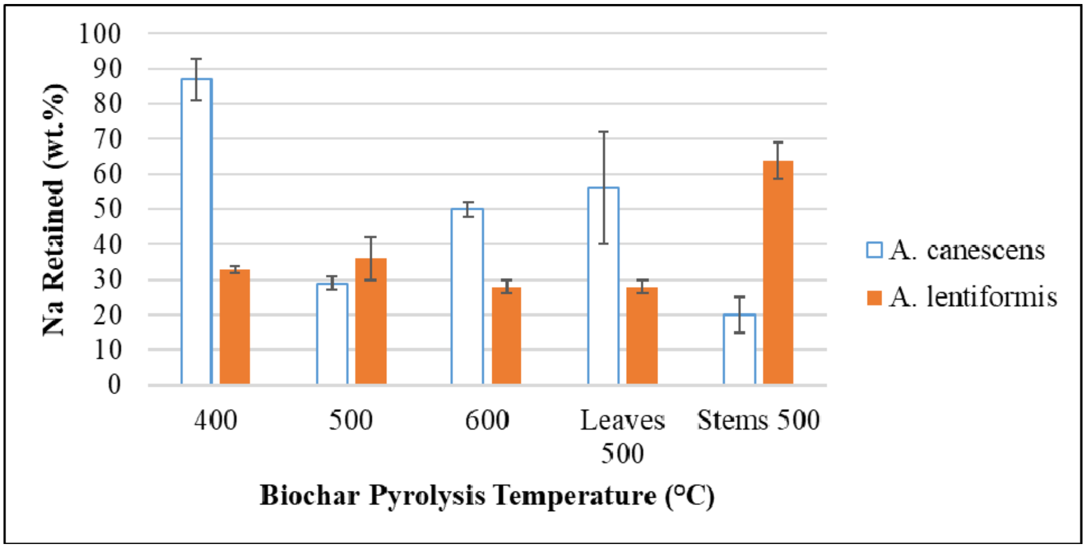

Figure 16.—Percent of sodium retained in biochars after leaching with 5 sample volumes of water. Error bars indicate one standard deviation (n = 3).

Biochar Anions

Preliminary anion quantification showed the presence of chloride, bromide, nitrate, sulfate, and phosphate in the halophyte biochar leachates, with conflicting results for the presence of nitrites. Plans are being developed to re-analyze all of the samples. Chloride had the highest concentrations in all the biochar leachates samples except for leachates of *A. canescens* biochar produced at 400 °C, which was relatively low in chloride. Overall, the trend for anion concentration was: chloride > bromide > sulfate > nitrate > phosphate.

CONCLUSIONS

Principal Findings

The principal findings of this exploratory study were that:

- *Atriplex lentiformis* contains more total salt and has a higher sodium-to-potassium ratio than *Atriplex canescens*.
- For a given pyrolysis temperature, *Atriplex canescens* biochar retains more of its salt content after short-term leaching compared to *Atriplex lentiformis* biochar.
- Salt retention is impacted by pyrolysis temperature: relative retention of Ca and Mg increased at 600°C, while a trend was less clear for Na and K.
- Biochar derived from the leaves of the halophyte biomass contained much more salt than biochar derived from the stems.
- Biochar leachates contained higher amounts of salts at the beginning of leaching, with concentration reducing as leaching continued, as expected from diffusion mass transfer.

Principal Conclusions

Atriplex lentiformis has a higher potential as a salt-uptake plant as its biomass contains higher levels of total salt, and a higher relative fraction of sodium. If only part of the plant were chosen for salt removal, the leaves are a better candidate than the stems. Pyrolysis reduces the total solid mass to approximately one-third of the original dry biomass, concentrating the salts in the biochars. Salts in biochar are susceptible to short-term leaching, with the highest fractions of salt being removed in water in the first few sample volumes. There is potential to retain a substantial fraction of salt in the short-term, and that fraction is affected by pyrolysis temperature. Higher pyrolysis temperatures may improve the retention of Ca and Mg salts; 400 °C appears to give the highest retention of K and Na, but more data are needed to confirm the trend.

A product of this research included an MS thesis in Water Science and Management (Sarpong 2017).

RECOMMENDATIONS

Recommendations for Additional Research

Leaching measurements in this study only considered short-term leaching (5 sample volumes), Leaching phenomena would have, therefore, included equilibrium and diffusion mass transfer limitations. More information is needed about the equilibrium concentration of salts in the biochars in the presence of water to estimate the potential for long-term salt immobilization.

Acid digestion of the biomass and biochar samples provides information about the total amount of alkali and alkaline earth metals. Use of microscopy techniques, such as scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), can provide more information about the relative distribution of different elements within the biomass and biochar. This information can elucidate the likely mechanisms of mass transfer and the effects of pyrolysis on those mass transfer mechanisms.

Biochars’ effects on soil fertility are a function of several char characteristics in addition to salt/nutrient content. Soil amendment and plant growth studies using halophyte-biochar amended soils are needed to understand how biochar salt content and water leachability affect soil-plant interactions. Some other properties of halophyte biochar may improve plant growth performance even if biochar’s ability to sequester certain salts might be limited.

Carbon and salts are concentrated in the biochars during pyrolysis. The stabilized carbon structure of the biochars may provide additional opportunities to gain benefits (i.e. carbon credits) from halophyte growth on concentrate-irrigated soils even if halophyte-derived biochars are not returned to the soils. The potential for carbon sequestration needs to be evaluated along with the potential for salt sequestration.

Summary

The objectives of this project were to identify the extent to which pyrolysis makes certain salts in plants less leachable, and to quantify the amount of salt within desalination concentrate-irrigated halophyte plants that might be immobilized in biochars. In this study, biomass from two Atriplex species, *A. lentiformis,* or big saltbush, and *A. canescens,* or four-wing saltbush, were treated by slow pyrolysis at 400-600 °C and the biochars leached with water using a constant heat permeameter. Alkali and alkaline earth metal cation quantification of the solids and the leachates were used to construct salt mass balances. Results indicate that calcium and magnesium are retained in biochars much more than sodium and potassium, that *A. lentiformis* biochar contains more salt but retains a lower fraction of that salt than *A. canescens*, and that salt retention in biochar is dependent on biomass species, plant component, and pyrolysis temperature.

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APPENDIX

TABLE A3.—Masses of biochar used for the leaching studies where the volume of the empty sample chamber was approximately 44 cc.

Biochar	Run 1 (g)	Run 2 (g)	Run 3 (g)	Average (g)
Atriplex canescens – 400 °C	11.36	11.74	11.75	11.62
Atriplex canescens – 500 °C	10.08	10.02	9.90	10.00
Atriplex canescens – 600 °C	12.06	12.00	11.75	11.94
Atriplex canescens leaves – 500 °C	8.60	8.20	8.30	8.37
Atriplex canescens stem – 500 °C	12.80	12.60	12.50	12.63
Atriplex lentiformis – 400 °C	8.88	8.59	7.92	8.46
Atriplex lentiformis – 500 °C	8.68	8.89	8.85	8.81
Atriplex lentiformis – 600 °C	10.00	9.80	10.20	10.00
Atriplex lentiformis leaves – 500 °C	7.20	7.00	7.00	7.07
Atriplex lentiformis stem – 500 °C	9.40	9.50	9.10	9.33

TABLE A2.—Alkali and alkaline earth metals in *A. canescens* biochars before and after leaching with water. (± = one standard deviation, n = 3)

Pyrolysis temperature/ component	Cation	Biochar (mg/g)	Leached biochar (mg/g)				Mass leached (mg/g)	% retained
			Run 1	Run 2	Run 3	Mean		
400 °C	Ca	4.4	4.0	3.8	3.9	4.0 ± 0.1	0.4	91 ± 3
	Mg	4.2	3.3	3.4	3.6	3.4 ± 0.1	0.8	80 ± 3
	K	20.9	15.5	15.5	16.2	15.7 ± 0.4	5.2	74 ± 2
	Na	0.8	0.7	0.7	0.6	0.7 ± 0.05	0.1	87 ± 6
500 °C	Ca	14.1	13.3	10.7	9.6	11.2 ± 0.8	2.9	79 ± 6
	Mg	9.4	8.3	7.2	6.4	7.3 ± 0.5	2.1	77 ± 5
	K	59.6	27.4	24.6	24.9	25.6 ± 0.5	33.9	43 ± 1
	Na	12.4	4.1	3.2	3.5	3.6 ± 0.2	8.8	29 ± 2
600 °C	Ca	8.3	7.4	8.5	9.2	8.4 ± 0.9	-0.1	100 ± 11
	Mg	6.8	6.4	7.1	7.7	7.1 ± 0.7	-0.3	104 ± 10
	K	42.1	29.8	30.6	30.3	30.2 ± 0.4	11.9	72 ± 1
	Na	0.7	0.4	0.4	0.3	0.4 ± 0.02	0.3	50 ± 2
Leaves	Ca	23.4	19.8	20.0	27.0	22.3 ± 4.1	1.1	95 ± 17
500 °C	Mg	14.2	11.6	12.4	17.0	13.7 ± 3.0	0.5	96 ± 21
	K	93.9	43.4	47.2	55.0	48.5 ± 5.9	45.4	52 ± 7
	Na	1.8	0.9	0.9	1.4	1.0 ± 0.3	0.8	56 ± 16
Stems	Ca	8.8	3.2	3.0	3.2	3.2 ± 0.2	5.6	36 ± 2
500 °C	Mg	6.6	4.0	3.8	4.0	4.0 ± 0.2	2.6	61 ± 3
	K	39.3	19.8	19.5	17.7	18.9 ± 1.1	20.4	48 ± 3
	Na	0.4	0.11	0.07	0.06	0.08 ± 0.02	0.3	20 ± 5