

**TRACE ELEMENT COMPOSITIONS OF BRINE IMPACTED SOILS AND
PRODUCED WATER IN OSAGE COUNTY, OKLAHOMA**

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Abstract

Current brine remediation techniques focus on salt removal as the primary goal. However, residual disturbance to the vegetation is a common characteristic of remediated sites. The purpose of this research is to identify potential brine-induced, elemental phytotoxins that could persist in the soil after a successful removal of the sodium chloride salt. Awareness of these phytotoxins could lead to more thorough remediation techniques that draw impacted soils closer to a pristine state. Twenty soils, representing a variety of stages of brine contamination, and three brine samples were investigated. Of the elements identified in brine-impacted soils, most appeared to follow the trend of the salt component of brine in that higher concentrations were found in non-remediated soils than in remediated ones. Historic brine scars typically contained the highest levels of both salt and identified elements, while pristine prairie soils had the lowest. One identified element did not follow this trend. Boron levels remained significant in all soils other than those from unimpacted prairie. In other words, boron was resistant to standard brine remediation techniques. This is significant because boron is a known phytotoxin.

Introduction

Current produced water (brine) remediation techniques focus on salt removal as the primary goal. Brine impacted soils are typically remediated by increasing soil permeability with organic matter, and perhaps gypsum, to allow salt to wash out of the soil toward an appropriate receptor (a subsurface drainage system, for example) (Carter 2002). These methods have been shown to be effective in sufficiently reducing salinity to allow for re-vegetation of a contaminated area. However, this re-growth could be stunted or altered by the presence of

harmful compounds introduced by brine that are resistant to these practices. Ignoring such phytotoxins and the damage they could inflict may result in the long-term inhibition of growth of desirable plants. Furthermore, there may be a return of vegetation to a once-contaminated area but the plant community may not be as diverse, abundant, or healthy as in pristine areas (Ross 1994).

Produced water composes the largest volume of waste emitted from oil and gas production activities. For onshore oil production, over 90% of produced water is reinjected into subsurface formations while offshore, it is discharged into the surrounding seawater (Ray 1992). Due to the immense volume produced and the necessity of handling and disposing of it, research has been conducted to characterize the chemical makeup of produced water and its corresponding hazards (Jacobs 1992). Although the composition of produced water is dependent on location and the effectiveness of the oil/water separation process, brines can be expected to contain a mixture of complex inorganic and organic components. The majority of in-depth analyses of these components and their corresponding toxicities have dealt with offshore produced water as it poses the most immediate threat to the adjacent environment (Tibbetts 1992). However, there is a significant gap in the literature concerning the ecotoxicological potential of onshore produced water, especially with regard to native, non-agricultural plant communities.

The purpose of this research is to identify potential brine-induced, elemental phytotoxins that could persist in the soil after a successful removal of the sodium chloride salt. Awareness of these phytotoxins could lead to more thorough remediation techniques that draw impacted soils closer to a pristine state. The first goal of this project was to identify which components of brine were suspected of being phytotoxic. Secondly, the phytotoxins impervious to current remediation

techniques were determined by analyzing the concentrations of these suspect elements in soils with various degrees of impact from produced water. For the purpose of this research, the definition of a phytotoxin is any substance that inhibits plant growth (Ross, 1994).

The degree of toxicity of a given compound may differ between various plants (Ross, 1994). Additionally, some compounds are only harmful above a particular concentration, and again this concentration may be plant-specific. For example, trace amounts of Cu, Zn, Fe, and Mn are vital for plant development while high amounts are generally inhibitory to plant health. In short, different plant species possess different thresholds of tolerance to the presence of phytotoxins in the soil. The effect of phytotoxins at the cellular level may include obstructing, denaturing, or inactivating enzymes, displacing and/or replacing important metal ions, and disturbing the proper function of cell membranes and organelles. The symptoms associated with this phytotoxicity include reduced cellular photosynthesis and respiration, water stress, wilting, and reduced ion selectivity in roots as a result of an alteration of the cytoplasm and plasma membrane. Several factors can determine whether various symptoms result, including: the plant species itself, various environmental stresses, and the detection technique utilized (Ross 1994). The literature is relatively silent about the relative phytotoxicities of different elements on native plant species, with most attention being devoted to agricultural species. While this current work does not explicitly define any element as a phytotoxin, it is intended to contribute to a growing awareness of the response of native plant communities to environmental contamination.

Materials and Methods

Site History:

All samples used in these experiments were obtained from throughout the Tallgrass Prairie Preserve, a 39,000-acre nature preserve located in Northeastern Oklahoma. The Nature Conservancy purchased the former oil field in 1989 for the purpose of restoring what was previously rangeland to the native tallgrass ecosystem which was once predominant in the Flint Hills region of northeastern Oklahoma and central-eastern Kansas. The primary means The Nature Conservancy accomplishes this goal is through a management plan consisting of bison grazing and prescribed burning. This plan is meant to mimic what would have been the natural occurrences of the historic tallgrass prairie as closely as possible. However, active petroleum production still continues on the Preserve. Accommodating both resource extraction and ecosystem restoration has been the impetus of a great deal of research between the University of Tulsa and the Nature Conservancy in the last decade.

Sampling Protocol:

A total of twenty sites were sampled, and these sites fall into four classifications (Table 1). The first classification applies to unimpacted pristine prairie sites used as the controls for the experiment. These produce a model of what an uncontaminated tallgrass soil should be composed of and what remediated sites should ideally return to. Seven of such sites were sampled. The second classification applies to historic brine scars, which are areas of non-remediated spills dating back as far as the early 20th Century. These sites are often the result of multiple contamination events. Five of these historic brine scars were sampled. The third classification applies to recent brine spills that have been remediated. These provide information as to which potential phytotoxins are carried away with salt during remediation and which

remain. Three of these sites were sampled. The fourth classification applies to recent brine spills that have not been remediated. Five of such sites were sampled.

In addition to soils samples, three liquid brine samples were taken directly from pump jacks at locations distributed across the Tallgrass Prairie. These samples provide the elemental makeup of the brine prior to contaminating the soil.

Soil Preparation

Sampling proceeded with five-fold composite samples taken at each research site. For each site, five holes were dug 15 cm deep at random locations, yielding roughly 60 kg (total) of sub-sample soil for each site. These sub-samples were then combined to form the composite sample that was then subjected to further testing. Each sub-sample was bagged, labeled and refrigerated at 4 C after sampling until use (no more than 4 days). Because the composite samples were composed of varying soils from each site, the soil had to be first homogenized before determining overall soil composition. Each soil sample was dried at 150 C for six hours to facilitate better grinding. Each was initially ground to a fineness of ≤ 150 microns using an automatic soil grinder (Cole-Parmer® Analytical mill, 110 VAC/60 Hz EW-04301-00). Due to mechanical malfunctions, a manual grinder was used for remaining samples. Grinding creates more surface area for future dissolution of the soluble components of the soil. From each homogenized sample, 25 grams of soil was dried at 150 C for four hours in order to remove any moisture that may have accumulated during the grinding process.

Extraction Procedure

The first step in the extraction procedure was to create a soil solution consisting of 5.0 grams of soil combined with 50.0 mL of high purity de-ionized water in a 50.0 mL plastic centrifuge tube. These solutions were sonicated at high power for one hour in a warm water bath (Branson 8210 Sonicator) in order to disperse the water-soluble components of the soils throughout the solution (Brady and Weil, 1999) . The insoluble components of the soil extracts were removed through a process of centrifugation and syringe filtration. Samples were centrifuged at 2,205 x g for 30 minutes. The supernatant was decanted and 15.0 mL were filtered through 0.45 micron filters (Acrodisc 37, Gelman Sciences). Ten mL of the resulting material were filtered a second time. This second filtration utilized 0.20 micron filters (Acrodisc 13 CR, Gelman Sciences) .

Preparation of the brine samples followed the same steps as above with the exception of an initial pipetting step. The brine samples contained a mixture of both crude oil and produced water. Therefore, the residual oil had to first be removed from the surface of the brine sample before further extraction steps could occur. The oil/brine mixture was allowed to settle at room temperature for approximately one hour to allow for phase separation. The oil was then gently hand pipetted from the surface. If phase separation was proceeding slowly, gentle centrifugation was applied to the mixture in order to encourage the segregation of the hydrocarbon from the accompanying produced water. The collected hydrocarbon was discarded and the produced water was diluted in a similar fashion as the soil samples. Initial brine dilutions were made by adding 5.0 mL of produced water to 45.0 mL of doubly de-ionized water.

The resulting brine and soil solutions were analyzed using inductively coupled plasma mass spectrometry (ICP-MS; Perkin-Elmer DRC II). Due to the sensitivity of the machine, coupled with the high concentrations of sodium and chloride in the samples, 1:1,000 dilutions

were required for the soil extracts and refined brine samples. Dilutions were made using high purity doubly de-ionized water. Salt concentrations were also measured indirectly by determining the conductivity of each solution. Given the small volume of the solution, a handheld conductivity probe was used.

Discussion

The goal of this project was to discern which components of produced water may be responsible for the recalcitrant phytotoxic effects found at sites of brine contamination. This study involved 20 sites and represented soils ranging from historic brine scars to remediated recent spill sites. Pristine, unimpacted soils were also analyzed. Three raw brine samples provided a comparison to the soils, in order to determine which residual soil elements were considered suspect of phytotoxicity.

The initial stage of this study involved the analysis of the components of raw brine. Seven major and eight minor elements were isolated from produced water samples (Tables 2 and 3). Elements were classified as “major” based on concentrations greater than 100 mg/L in the produced water and “minor” elements on concentrations less than 100 mg/L. Of the major elements, Mg gave the highest range of concentrations (5834-7882 mg/L) and Ti and Ba the lowest (0-104 and 37-103 mg/L, respectively). Of the minor elements, Li gave the highest range of concentrations (8.1-15.4 mg/L) and As the lowest (0.1-0.5 mg/L). There was no apparent pattern of element distribution in that no one brine sample consistently had more or less of the identifiable elements in comparison to the other two samples.

The concentrations of the various brine elements then had to be compared to concentrations of elements extracted from soils that were recently brine-impacted (both

remediated and non-remediated) and historic brine scars. Unimpacted prairie soils would provide the comparison soil composition that would allow us to determine whether remediation had lowered potentially phytotoxic compounds to near normal levels.

Certain elements, such as magnesium and calcium, were detected at relatively high concentrations in the brine samples (Table 2). However, these elements are common in non-contaminated soils as well as in the biomass of plants (Brady 1999). Therefore, these elements were not primary suspects as the causative agents of phytotoxicity. Other elements that are not found in great abundance in the soil, such as strontium and bromine, appeared at relatively high concentrations in brine (Table 3). When compared with their soil concentrations (data not shown), though, most of these elements displayed the trend established by soil conductivity. That is, their concentration is related to the presence of the brine salt. As salt levels decreased, so did the levels of strontium and bromine. The conclusion is that their introduction is clearly associated with the presence of brine and they respond to salt removal remediation.

Measuring the conductivity of the soil samples was meant to provide a relative measure of soil ions. By comparing this model to the trends of individual elements within the soil, we could determine whether these elements responded to or resisted salt-removal remediation techniques. The model we generated for soil conductivity shows a progressive increase in soluble salts from least to greatest beginning with unimpacted sites followed by recent remediated spills, recent non-remediated spills, and historic brine scars (Figure 1). It is not surprising that a historic brine scar (which is often the result of multiple contamination events) would contain higher concentrations of soluble salts than more recent spill sites that are often the result of a single release event. It also is not surprising that a recent, non-remediated spill site would contain more soluble salts than a remediated one. Therefore, for an element to be considered brine-induced it

should demonstrate relatively high concentrations in historic brine scars and non-remediated brine spills as compared to pristine soils. Further, for an element to show a response to salt-removal remediation, the element should demonstrate relatively low concentrations within a remediated, recent brine spill site in comparison to its concentration in brine scars or non-remediated brine spills.

An analysis of bromine in soils displayed a trend very similar to that of salt (Figure 2). The levels of the element in historic brine scars and recent, non-remediated brine spills were comparatively higher than those in pristine areas and remediated brine spills. Thus, Br concentrations in the soils were likely a result of brine exposure. Non-remediated sites, both historic and recent, also exhibited greater variation in concentrations compared to remediated and pristine sites. In contrast, the levels of Br in remediated sites approached those of pristine areas. This trend indicates that Br had a positive response to salt-removal remediation efforts.

Strontium displayed the same concentration pattern as Br (Figure 3). There were extremely high concentrations in historic scars. The concentration in recent, non-remediated sites was four times that of unimpacted soils. Greater variation in these concentrations was also found in the contaminated sites, following the pattern observed with Br. Again, remediation of the recent brine spill reduced levels of Sr close to levels found in unimpacted prairie. Furthermore, there was more consistency in Sr concentrations among remediated sites. Increased consistency of element concentrations between soil samples was also indicative of a generally positive response to salt-removal remediation.

Using bromine and strontium as examples, it can be deduced that most elements showing a significant concentration in both brine and brine-impacted soils would return to near-normal levels following remediation. This means that potentially phytotoxic elements that showed a

decrease in concentration after remediation were removed by current remediation protocols. Each such element showed a clear signature of the brine in historic and recent spills, with elevated levels compared to unimpacted sites. These elements also showed significantly diminished concentrations following remediation. Therefore, we do not feel that these types of elements are responsible for the negative effects on vegetation that linger at remediated sites.

In contrast, boron was the one element analyzed that did not follow the above pattern established by the other elements (Figure 4). Boron showed the signature of the brine, with elevated concentrations in both historic and recent brine spills. Historic scars showed a wide range of values peaking at nearly 3 mg/kg. In contrast to the other analyzed components of brine, boron persisted at high levels in remediated sites (soil classification “3”). Whereas soil washing was able to reduce the concentration of other brine elements, boron concentrations were not decreased in response to the salt-removal techniques.

The apparent recalcitrant nature of boron is interesting because the element is known to be phytotoxic to some plants. Boron is toxic to rice at soil concentrations greater than 4mg/kg (Dobermann, 2000). Soil levels of boron in remediated sites approached this concentration. While phytotoxicity thresholds vary from plant to plant, residual NaCl from brine contamination may weaken the defense mechanism in plants growing in salt-affected areas (Salisbury and Ross, 1992). This may make them more susceptible to the toxic effects of boron when the element is present at lower concentrations than would normally cause a negative response. It is for this reason that boron is suspected of being a significant phytotoxic component of brine.

Conclusions

Brine spills introduce a number of various compounds into the soil. Some of these compounds are introduced in significantly higher amounts than levels found in unimpacted soils. Salt remediation works to diminish the presence of many of these elements. However, there are exceptions to this trend. Such elements show no response to current remediation techniques. Some of these recalcitrant compounds, such as boron, are known to be toxic to plants. Their toxic effects could be compounded by the presence of any sodium chloride persisting in contaminated soils.

Deconstructing produced water exposed its composition to be far more than simply sodium chloride-impacted water. Contamination by produced water introduces a myriad of elements into the soil. However, boron is the only element detected thus far that resists current salt-removal remediation techniques. This element is known to be phytotoxic at levels found within the test samples. Thus, boron will be the focus of future research attention.

Future Work

Future work will require additional trials of the previous experiment to identify other suspect elements. Additional testing will also reinforce our initial findings. If further experimentation uncovers new compounds of interest, element-specific extraction procedures will be implemented to enhance the recovery of them for analysis. Future work would include determining how much of a suspected phytotoxin is available for uptake by plants. Additionally,

investigations will be performed to discern the specific effects of the identified elements on tallgrass prairie climax grasses and salt-stressed grasses.

Acknowledgements

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Table 1. Classification of Sample Sites

Classification	Description	# of Sites
1. Pristine	Areas unimpacted by oil production	7
2. Historic Brine Scars	Areas subjected to long-term contamination with brine without clean-up efforts	5
3. Remediated Brine Spills	Areas affected by recent brine spills that have been successfully remediated	3
4. Non-remediated Brine Spills	Areas affected by recent brine spills that have not been remediated	5

Table 2. Major Elements in Produced Water (mg/L). The following elements were detected in the produced water samples at concentrations ≥ 100 mg/L.

<u>Brine Sample</u>	<u>Mg</u>	<u>K</u>	<u>Ca</u>	<u>Ti</u>	<u>Sr</u>	<u>Ba</u>	<u>Br</u>
SW	5834	336	2588	84	1115	103	1860
E	7882	362	2977	104	2136	37	2662
NW	6106	509	2349	0	1037	80	1597

Table 3. Minor Elements in Produced Water (mg/L). The following elements were detected in the produced water samples at concentrations ≤ 100 mg/L.

<u>Brine Sample</u>	<u>Li</u>	<u>V</u>	<u>Mn</u>	<u>Se</u>	<u>Rb</u>	<u>B</u>	<u>I</u>	<u>As</u>
SW	10.6	0.3	1.6	0.4	0.8	3.6	1.0	0.1
E	8.1	0.4	1.5	0.5	0.8	1.7	1.3	0.5
NW	15.4	0.3	2.3	0.3	1.2	7.0	0.9	0.1

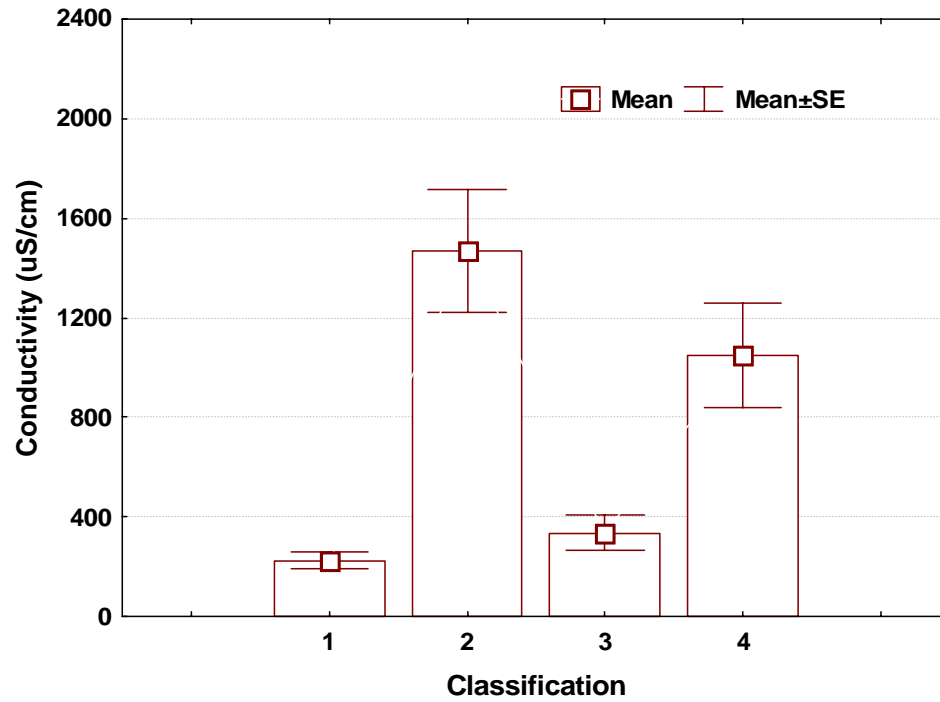


Figure 1. Conductivity of Soil Extracts. Measurements are on a per gram of dry soil basis.

Classification code: 1= unimpacted prairie
 2= historic brine scars
 3= recent, remediated brine spills
 4= recent non-remediated brine spills

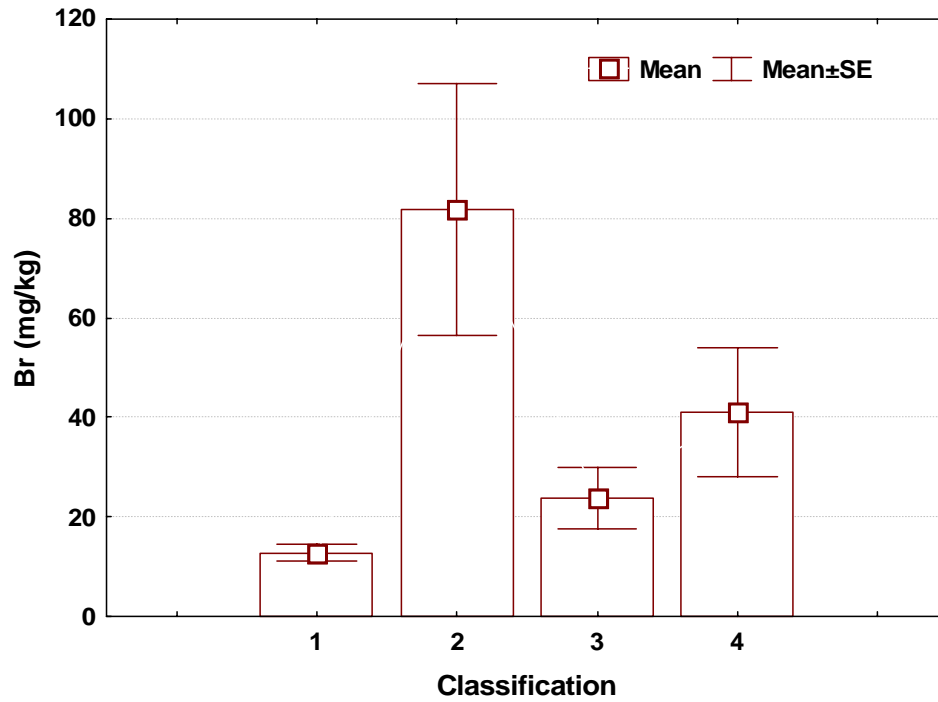


Figure 2. Bromine Concentration in Soils based on a per gram of dry soil basis.

Classification code: 1= unimpacted prairie
 2= historic brine scars
 3= recent, remediated brine spills
 4= recent non-remediated brine spills

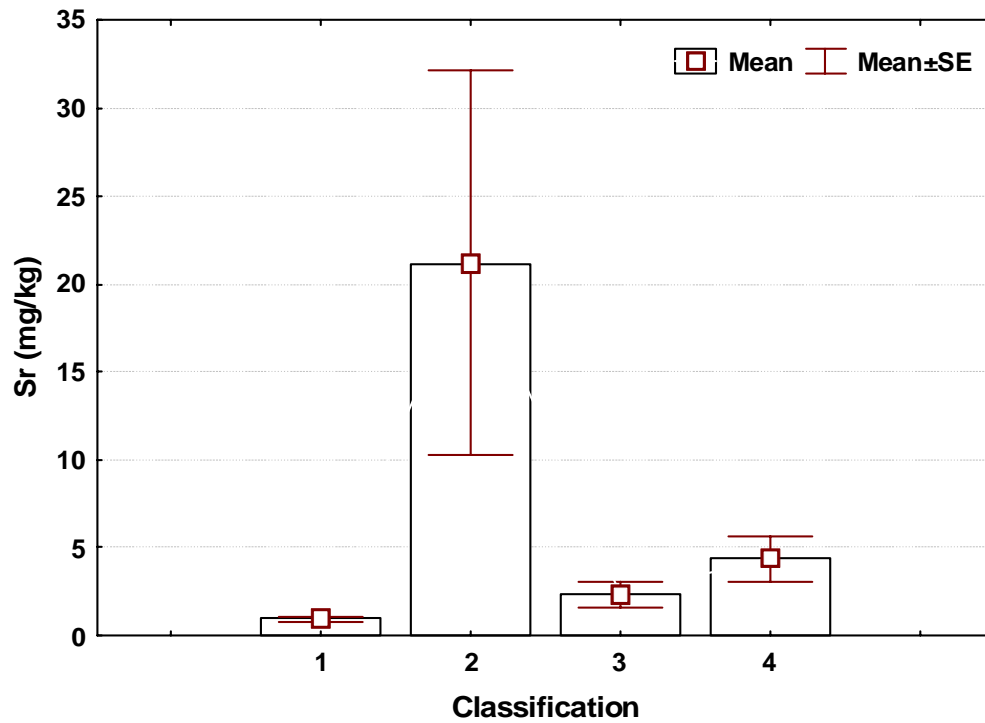


Figure 3. Strontium Concentration in Soils (based on dry weight). Measurements are on a per gram of dry soil basis.

Classification code: 1= unimpacted prairie
 2= historic brine scars
 3= recent, remediated brine spills
 4= recent non-remediated brine spills

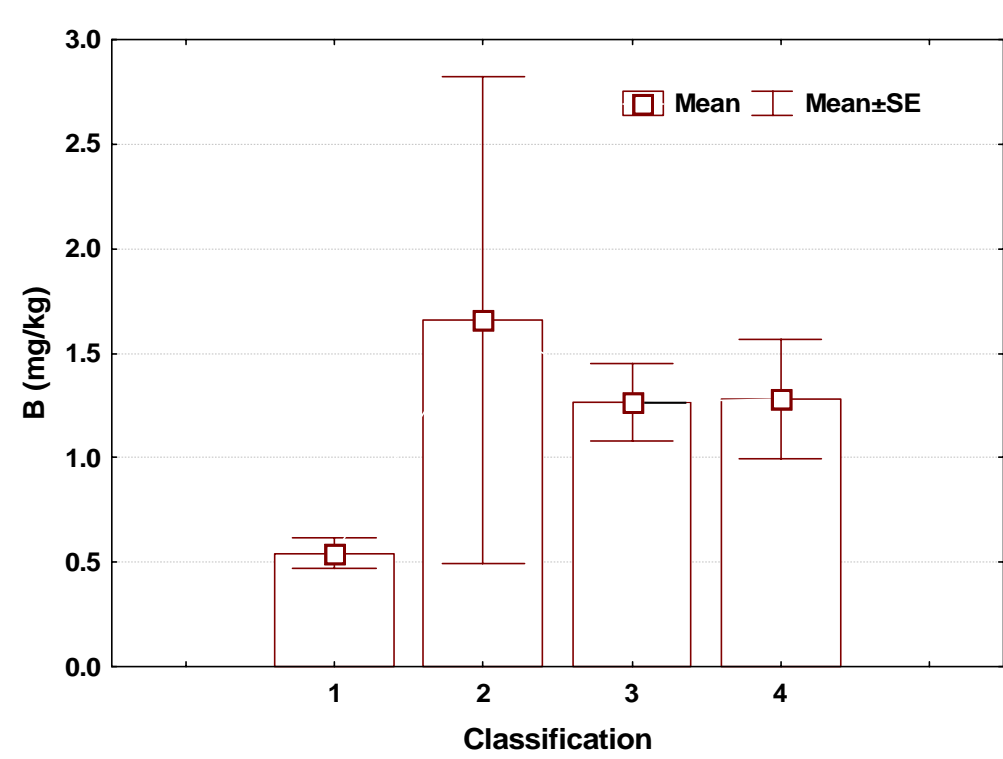


Figure 4. Boron Concentration in Soils (based on dry weight). Measurements are on a per gram of dry soil basis.

Classification code: 1= unimpacted prairie
 2= historic brine scars
 3= recent, remediated brine spills
 4= recent non-remediated brine spills