[PS]Soil Chemistry Analysis of Brine Contaminated Soils in West Texas, USA*

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Abstract

The focus of this project is to develop a basis for future remediation by investigating the changes in soil chemistry, mineralogy, and structure due to brine contamination at a historic site. The study area is a 14-acre brine contaminated kill zone, located about 14 miles south of San Angelo, Texas. The site is characterized by a lack of vegetation, salt crust, highly compacted soils, and low infiltration rates. Composite soil samples were collected from each section, as well as one from both upgradient and downgradient of the kill zone. Macro and micro nutrient analysis (i.e. total alkalinity, extractable calcium, chloride, total copper, extractable potassium, extractable magnesium, extractable sodium, nitrate, total phosphorous, pH, SAR, sulfate, and total kjeldahl nitrogen), Scanning Electron Microscopy (SEM), and X-Ray Diffraction (XRD) were used to characterize the soils. In the contaminated soils, concentrations of extractable sodium and chloride averaged 2,904 mg/kg and 6,086 mg/kg respectively, while the SAR averaged 25.89. XRD revealed that the dominant clay minerals in the background sample were kaolinite and halloysite. Kaolinite and halloysite were also the dominant clay minerals found in the brine contaminated soils. SEM images of the contaminated samples showed a drastic alteration in soil structure. The change in structure was caused by the excess sodium ions in the brine, which replaced the calcium and magnesium ions in the clays. The larger sodium ions increased the distance between clay particles, creating a repulsive force which pushed the clay particles apart, causing dispersion. Dispersion, in turn caused the plugging of the clay soils, which resulted in decreased infiltration rates and compaction. Overall, the clay mineralogy remained relatively constant after brine contamination, but the soil chemistry and structure were drastically altered.

References Cited

Robbins, C.W., and R.G. Gavlak, 1989, Salt and Sodium Affected Soils: College of Agriculture, University of Idaho, Moscow, Cooperative Extension Service Bulletin No. 703, 12 p.

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Abstract

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Study Area

- The purpose of this study was to examine the changes in soil chemistry, mineralogy, and structure likely caused by brine contamination at a historic site, to develop a basis for remediation.
- The study took place on a 14 acre kill zone in Tom Green County, Texas; located about 14 mi. south of San Angelo, Texas (Figure 1).
- The kill zone resulted from the disposal of brine water in a wood lined pit during the 1950's, creating a brine water plume that is migrating downgradient (NE) perpendicular to the terraces (Figure 2).
- The seven terraces are the result a previous remediation attempt during the 1980's.
- The study area sits on a talus slope underlain by Permian age rocks at a depth of ~30 ft.
- Resistivity surveys show the brine water plume extends ~23 ft. below the soil surface.
- The contaminated soils are dispersed and classified as saline sodic. They also exhibit low infiltration rates, a salt crust, a lack of vegetation, and are highly compacted.
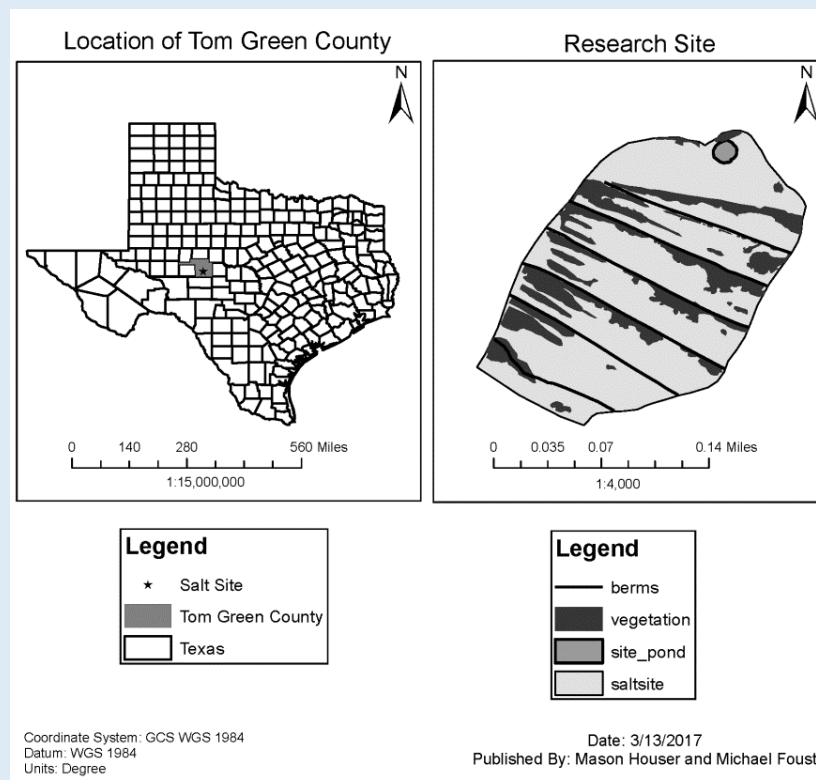
Figure 1: Location of research site.

Figure 2: Aerial photo of research site.

Methodology

- Soil samples were collected from five of the brine contaminated sections. Two background samples were also collected, one from both upgradient and downgradient of the kill zone.
- Samples were collected to a depth of 6 in. using two trowels and were composites; created by combining multiple samples from each section.
- Soil samples were air dried, labeled, and stored in plastic bags.
- They were analyzed using micro and macronutrient analysis, SEM, and XRD.
- Micro and macronutrient analysis were performed by Trace Analysis Inc.
- The results for the micro and macronutrient analysis were plotted on Ternary and Piper Diagrams by importing and then modeling the data in the program The Geochemist's Workbench.
- SEM and XRD analysis were performed by the Sul Ross State University Analytical Lab.
- Soil samples for SEM and XRD analysis were dried in a Quincy Model 30GC Lab Oven at about 142°F for one hour and then sieved.
- SEM samples were sputter coated with carbon using a Denton Vacuum Desk V Sputter Coater and Denton Vacuum Carbon Accessory.
- SEM analysis was performed using a JEOL JSM-6010LA Scanning Electron Microscope and InTouchScope navigation software.
- XRD analysis was performed using a Bruker X-ray powder diffractometer, DIFFRAC.EVA software, and the International Database for Diffraction Data.

Micro and Macronutrient Analysis

- Micro and macronutrient analysis included total alkalinity, extractable calcium, chloride, total copper, extractable potassium, extractable magnesium, extractable sodium, nitrate, total phosphorous, pH, SAR, sulfate, and total kjeldahl nitrogen.
- Concentrations of extractable sodium and chloride in the kill zone averaged 2,904 mg/kg and 6,086 mg/kg respectively (Table 1).
- The soil is classified as saline sodic as average SAR (25.9) is greater than 13, pH (7.62) is less than 8.3, EC (30.73 dS/m) is greater than 4 dS/m, and ESP (71.33%) is greater than 15% (Robbins et al. 1989).
- Typically, plants cannot grow if soil pressure exceeds 300 psi; however, average soil pressure in the kill zone was well over 500 psi.
- Overall, micro and macronutrient analysis revealed that there are many deficiencies and surpluses likely affecting plant growth and soil structure. However, the most problematic is probably the high concentration of sodium. Due to the excess sodium in the brine, sodium ions likely replaced the calcium and magnesium ions in the clays. Since sodium ions are much larger than calcium and magnesium ions, the distance between clay particles increased, creating a repulsive force which pushed the clay particles apart causing dispersion of the soil. Dispersion is problematic as it destroys soil structure, causing compaction, low infiltration rates, and the development of a salt crust, all of which are exhibited at the site (Robbins et al. 1989). These characteristics prevent plant growth and lead to erosion of the top soil.
- The replacement of calcium and magnesium ions by sodium ions is supported by the Ternary and Piper Diagrams in Figures 3-5, as they show high concentrations of sodium ions in comparison to the low concentrations of calcium, magnesium, and the other cations. The piper diagram in Figure 5 also shows the high concentration of chloride ions in relation to the other anions.

Table 1: Macro and Micronutrient Analysis

| Sample ID	Total Alkalinity mg/Kg as CaCO₃	Extractable Calcium mg/Kg	Chloride mg/Kg	Total Copper mg/Kg	Extractable Potassium mg/Kg	Extractable Magnesium mg/Kg	Extractable Sodium mg/Kg	Nitrate mg/Kg	Total Phosphorus mg/Kg	pH	SAR	Sulfate mg/Kg	Total Kjeldahl Nitrogen mg/Kg
SR 1	700	1310	6380	4.86	56.2	98.8	2310	93.1	187	7.13	16.6	207	<100
SR 2	1250	708	5220	4.95	68.4	52.7	2610	60.5	200	7.73	33.5	287	<100
SR 3 A	750	786	6030	4.91	67.5	84.1	2910	88.8	232	7.92	26.3	254	126
SR 3 B	600	811	6430	5.62	62.3	84.6	2970	86.0	215	7.78	26.5	253	<100
SR 3 C	750	777	5760	4.58	65.6	83.2	2850	82.5	212	7.39	25.9	214	<100
SR 4	750	701	5420	5.56	55.0	66.1	2870	68.9	253	7.69	27.7	61.4	126
SR 5	600	912	7360	6.51	67.6	69.7	3810	148.0	239	7.72	32.7	84.4	182
Average	771	858	6086	5.28	63.2	77.0	2904	89.7	220	7.62	25.9	194	
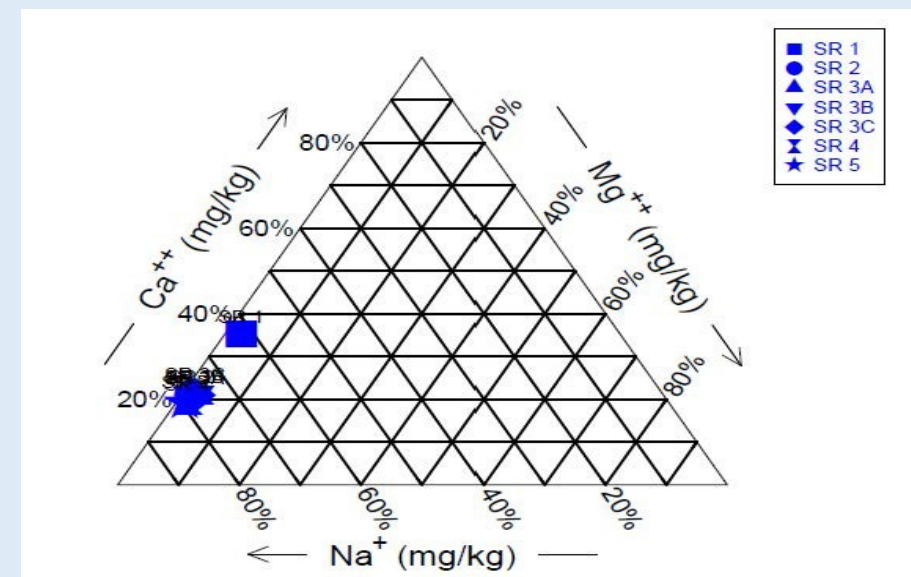
Figure 3: Ternary Diagram showing high percentages of Na⁺ in relation to the low percentages of Ca²⁺ and Mg²⁺ in the brine contaminated soil samples.
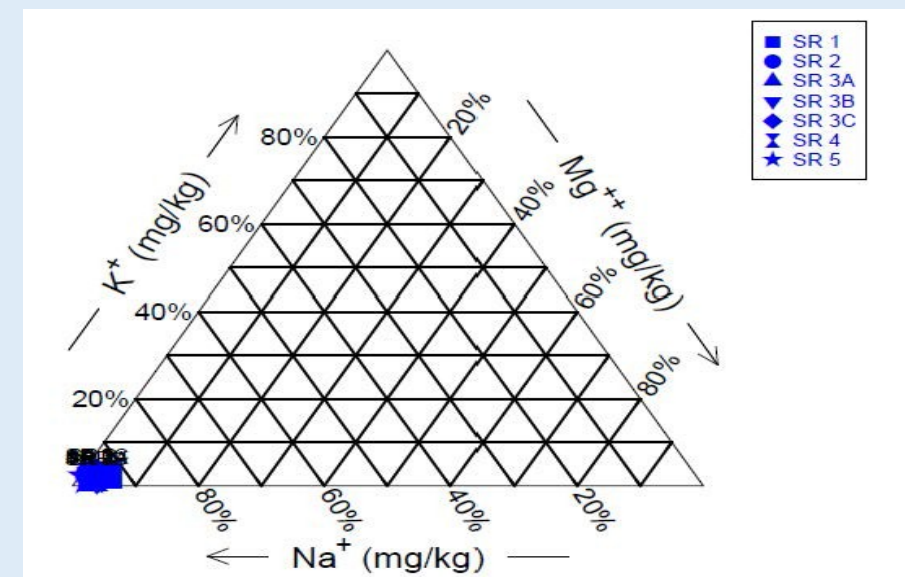
Figure 4: Ternary Diagram showing high percentages of Na⁺ in relation to the low percentages of K⁺ and Mg²⁺ in the brine contaminated soil samples.
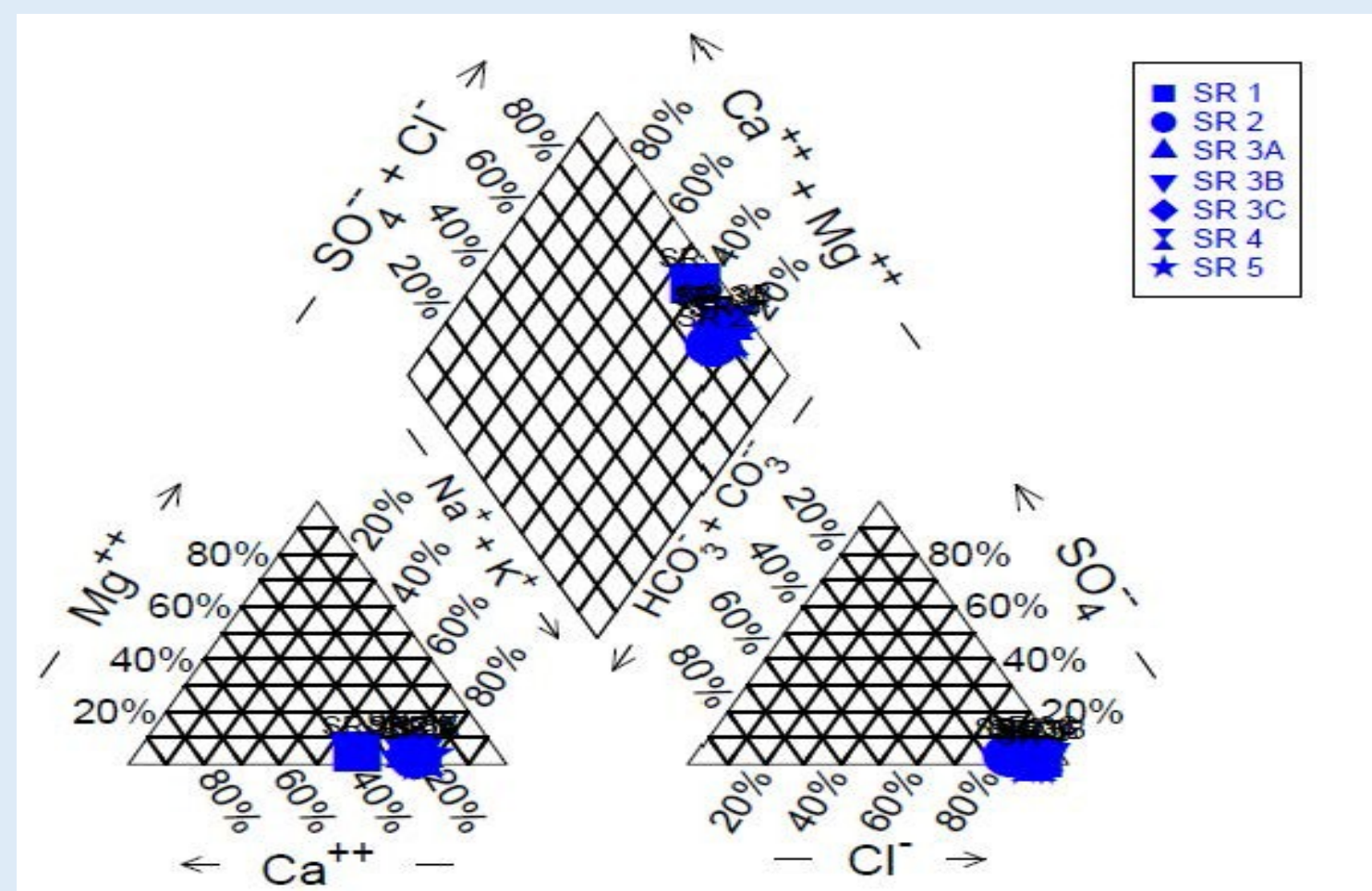
Figure 5: Piper Diagram showing the relationships between major cations and anions, most notably the high percentages of Na⁺ and Cl⁻ in relation to the other cations and anions present in the brine contaminated soil samples.

SEM Background Samples

- SEM analysis was performed on both contaminated and uncontaminated samples to develop a better understanding of the clay mineralogy and soil structure.
- The dominant clay minerals found in the background samples were kaolinite and halloysite.
- The kaolinite crystals in the background samples display distinctive layering and plate like geometry (Figures 6-8). Figure 6 shows that one of the kaolinite crystals had individual layers that averaged approximately 0.537 µm thick.
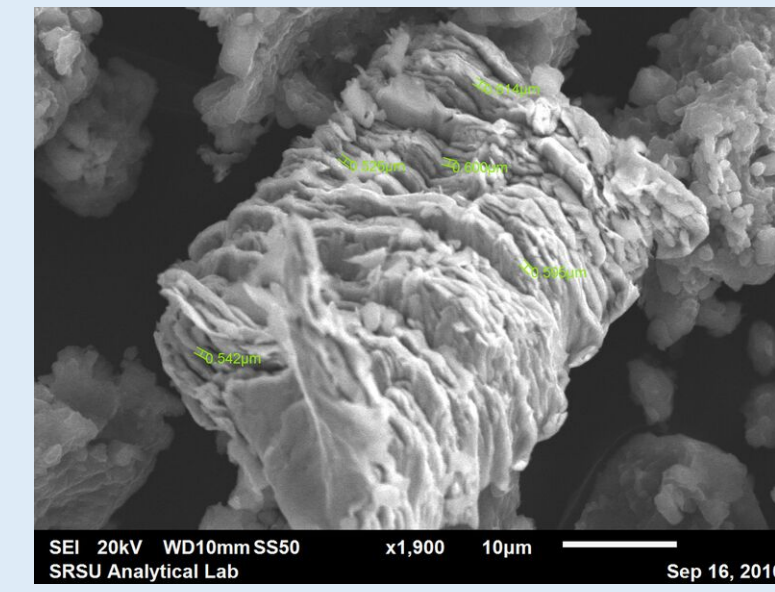- The halloysite nanotubes in the background sample are highly disordered (Figure 9).

Figure 6: SEM image from background sample showing the thickness of individual layers in a kaolinite crystal. The average thickness of the individual layers is approximately 0.537 µm.
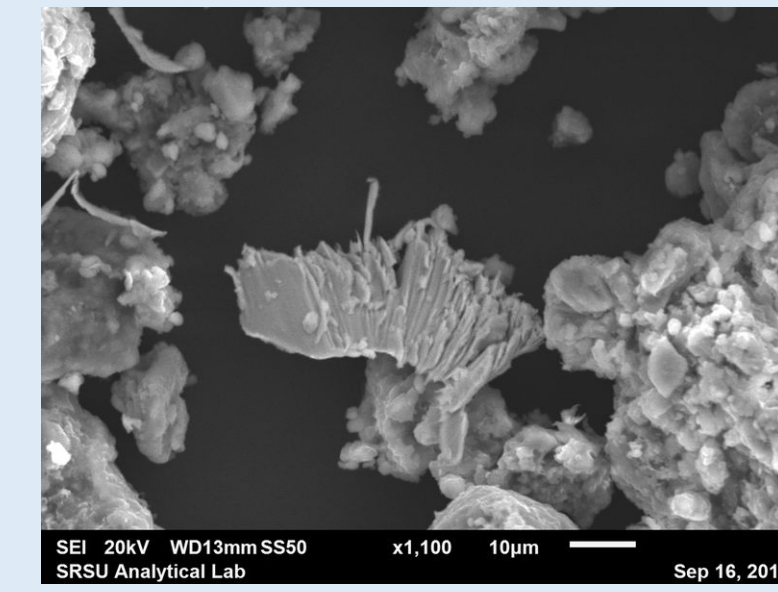
Figure 7: SEM image from background sample showing the distinctive layering and plates characteristic of kaolinite.
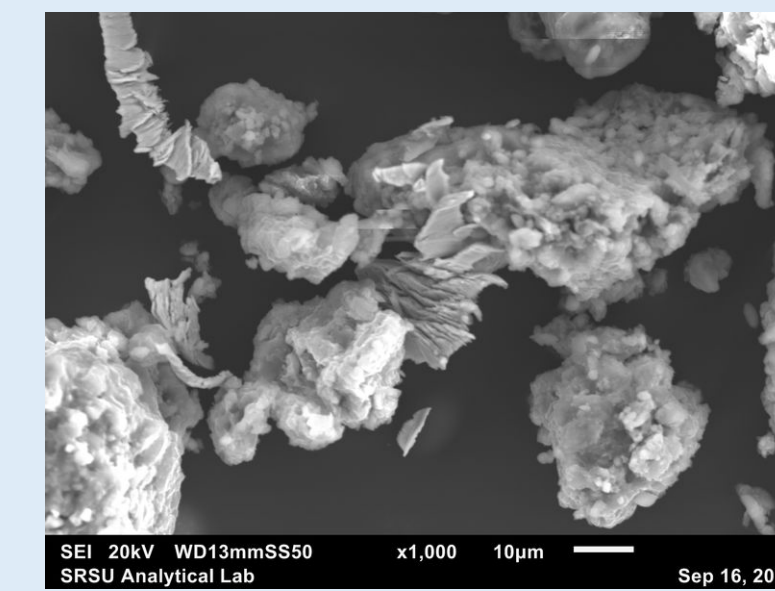
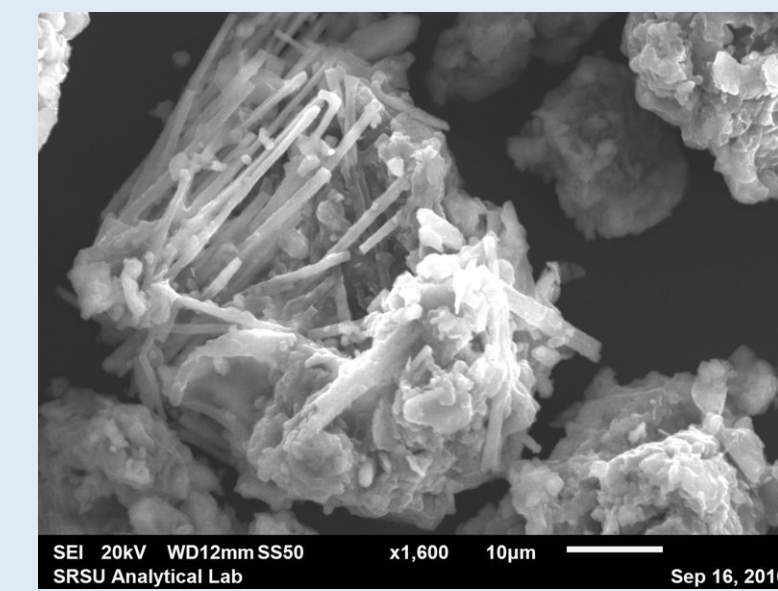Figure 8: SEM image from background sample showing kaolinite crystals.

Figure 9: SEM image from background sample showing highly disordered halloysite nanotubes.

SEM Brine Contaminated Samples

- SEM analysis of the brine contaminated samples revealed that kaolinite and halloysite are still the dominant clay minerals present in the soils.
- However, as seen in Figures 10-13 the brine contaminated samples show a drastic alteration in crystal structure, as the distinctive characteristics of the kaolinite and halloysite crystals found in the background samples are no longer visible.
- The destruction of the crystal structure was likely induced by the excess sodium ions in the brine, which caused dispersion of the clay soils, resulting in the collapse of the clay structure and the highly compacted soils exhibited at the site.
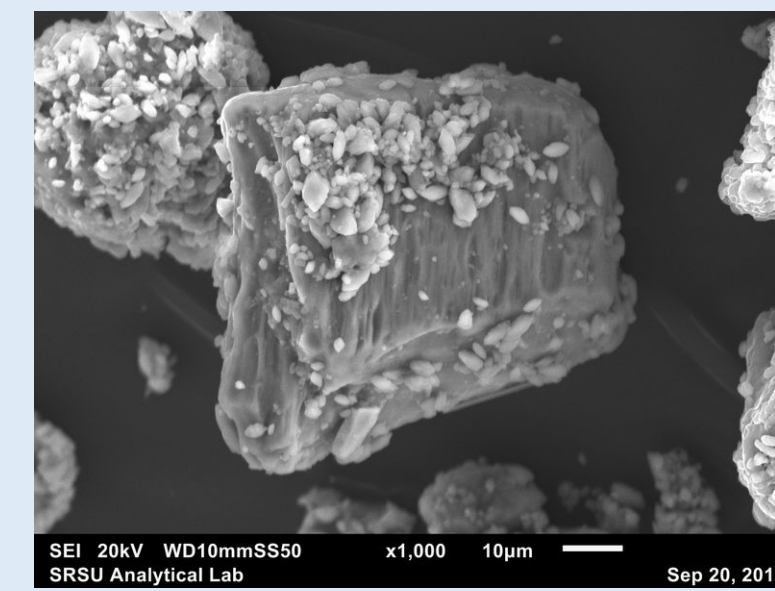
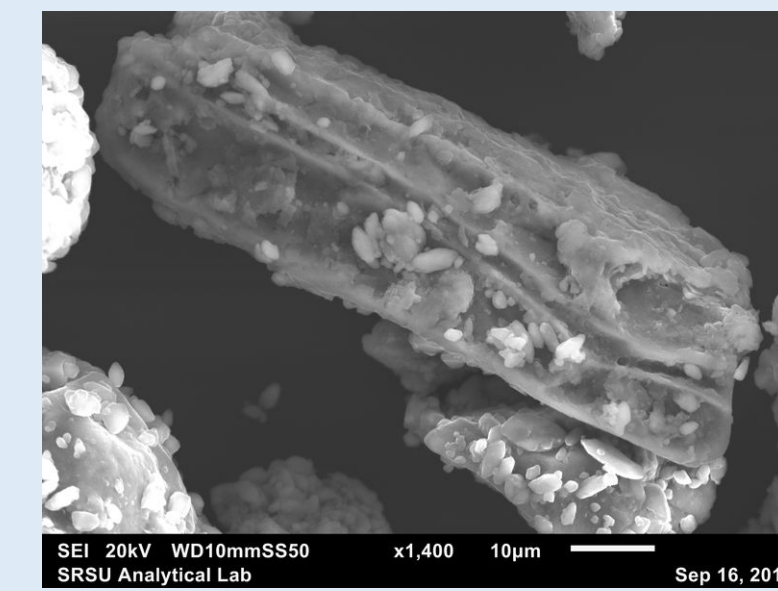Figure 10: SEM image from section 1 showing a compacted crystal.

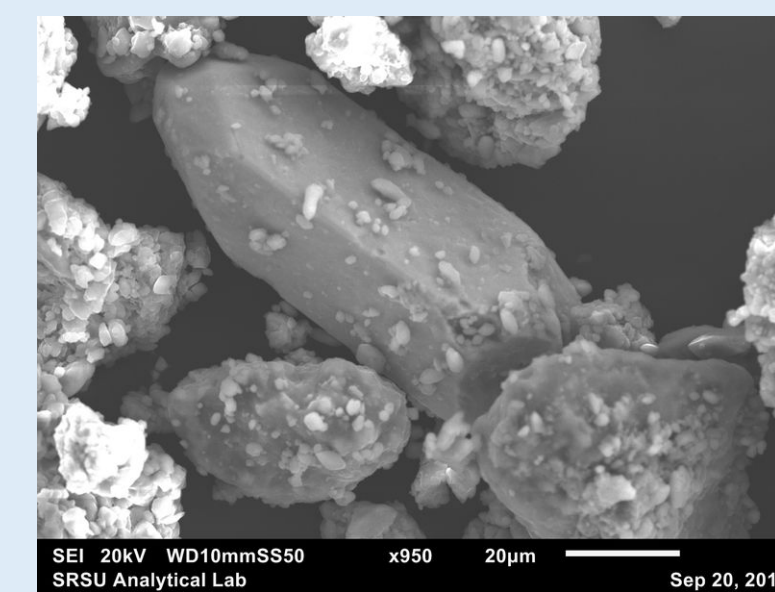Figure 11: SEM image from section 1 showing a compacted crystal.

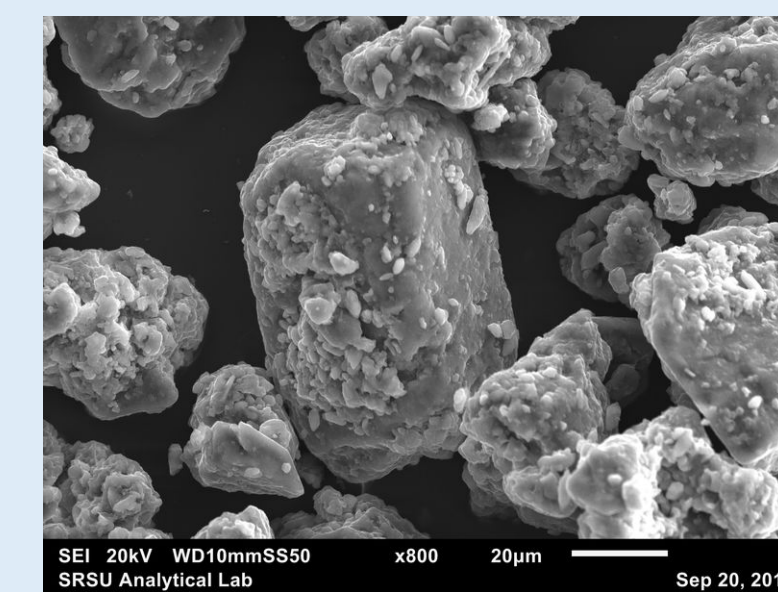Figure 12: SEM image from section 2 showing compacted crystals.

Figure 13: SEM image from section 3 showing compacted crystals.

XRD Analysis

- XRD analysis was used to quantitatively investigate the minerology of the soils.
- Quartz and calcite were found to be the most abundant minerals present in the contaminated and uncontaminated soils and one sample contained albite. However, as shown in Table 2 and Figure 14, kaolinite and halloysite are the dominant clay minerals present in both the contaminated and uncontaminated soils.
- The concentrations of kaolinite (3.6% - 21.9%) and halloysite (2.6% - 22.6%) varied considerably across the site, but no correlation was made due to the small number of soil samples.
- Overall, XRD analysis reveals that brine contamination likely had little affect on the minerology of the soil.

Table 2: XRD analysis by sample ID

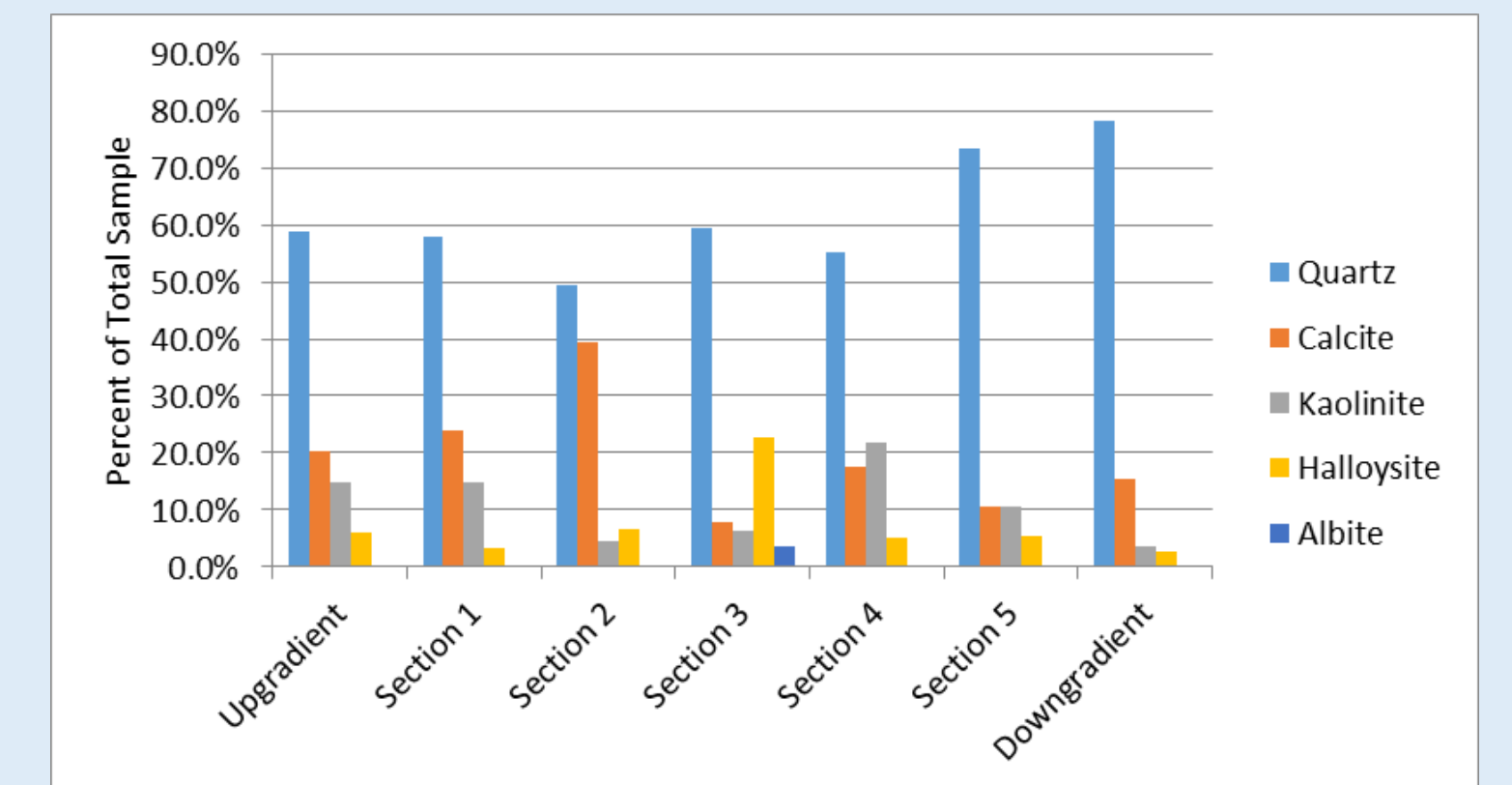|	Upgradient	Section 1	Section 2	Section 3	Section 4	Section 5	Downgradient
Quartz	58.7%	58.0%	49.3%	59.5%	55.2%	73.3%	78.3%
Calcite	20.3%	23.9%	39.5%	8.0%	17.6%	10.7%	15.5%
Kaolinite	14.9%	14.9%	4.5%	6.3%	21.9%	10.7%	3.6%
Halloysite	6.0%	3.3%	6.7%	22.6%	5.2%	5.3%	2.6%
Albite	0.0%	0.0%	0.0%	3.7%	0.0%	0.0%	0.0%

Figure 14: Graph depicting the change in composition of the soil samples, as one travels downgradient across the study area. See Figure 2 for locations.

Conclusions

- Micro and macronutrient analysis were used to quantify concentrations of nutrients such as sodium and chloride, leading to the classification of the contaminated soils as dispersed and saline sodic.
- SEM and XRD revealed that kaolinite and halloysite were the dominant clay minerals in both the contaminated and uncontaminated soils.
- SEM images showed a drastic change in soil structure due to dispersion likely induced by the excess sodium ions in the brine.
- Overall, brine contamination likely caused the drastic changes in soil chemistry and structure seen in the kill zone, while mineralogy remained relatively constant. This resulted in highly compacted soils, a lack of vegetation, a salt crust, and low infiltration rates.

Future Work

- Future work will include further analysis of the soils using X-ray Fluorescence (XRF) to identify any heavy metals that may be present in the soil.
- The results of this study will be utilized in a larger study involving the remediation of the site using halophytes, to help create the most effective strategy for remediation.
- The soils will be periodically tested using SEM, XRD, and XRF to identify any changes in soil chemistry, mineralogy, or structure.

Acknowledgements

References

Available upon request.