IMPACTS OF COALBED NATURAL GAS CO-PRODUCED WATER ON CROPLAND IRRIGATED SOILS IN THE POWDER RIVER BASIN, WYOMING¹

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Abstract: Water quality is a major concern with regard to development of coalbed natural gas (CBNG) in the Powder River Basin. Large quantities of water are being produced and discharged as a by-product in the process of releasing natural gas from coal. Current practices of discharging large volumes of water into drainage channels or using it to irrigate cropland areas has the potential to elevate salinity and sodicity in soils. Elevated salinity affects the ability of plants to uptake water to facilitate biochemical processes such as photosynthesis and plant growth. Elevated sodicity in irrigation water adversely affects soil structure necessary for water infiltration, nutrient supply, and aeration. Salinity and sodicity concentrations are important in that a sodic soil can maintain its structure if the salinity level is maintained above the threshold electrolyte concentration. In this study, cropland soil and CBNG water were treated with gypsum and sulfur. Plots were monitored to evaluate the effects of gypsum and sulfur on pH, electrical conductivity (EC), sodium adsorption ratio (SAR), and sulfate concentrations. Changes in soil chemistry due to the addition of different qualities of irrigation waters such as CBNG water and soil amendments were monitored using a split plot experiment. The CBNG water used for irrigation had an EC of 1380 µS cm⁻¹ and SAR of 24.3 mmol^{1/2} L^{-1/2}. Baseline and post treatment soil samples were collected to a depth of 60 cm within each study plot, analyzed, and characterized for chemical parameters. Comparisons between baseline and post irrigation soil chemistry data after one season indicated treatment of the irrigation water statistically increased (P<0.05) the rate at which Na^+ is moved through the profile. The addition of gypsum and sulfur as a water treatment and a soil amendment was the most effective in maintaining low SAR at the soil surface. Both EC and SAR statistically increased with all treatments in the top two sampling depths. Applying a leaching fraction at the end of each irrigation season should be tested for its effectiveness at moving Na⁺ below the rooting zone.

Additional Key Words: saline, sodic, sodium adsorption ratio, gypsum, sulfur, CBNG water

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Introduction

Natural gas consumption is at an all time high in the United States and is expected to grow by 50% in the next 20 years (U.S. BLM, 2003). Natural gas produced from coal seams accounts for approximately 10% of the current natural gas production in the United States (Ganjegunte et al., 2005). The Powder River Basin (PRB) in Montana and Wyoming is considered the most active area for coalbed natural gas (CBNG) production with an estimated reserve of 31.8 trillion ft³ (U.S. BLM, 2003)

Large quantities of water are being produced as a by-product during CBNG production (hereafter called CBNG water). In Wyoming, the U.S. BLM (2003) estimates that 366,000 ha-m of CBNG water will be produced from 2002-2017. CBNG water results from the drawdown of water in coal aquifers that is required to decrease hydrostatic pressure in the coal seam in order to release CBNG. Current methods of CBNG water disposal include impoundment, infiltration reservoirs, treatment, release into steam channels, and land application to enhance forage and field crops production (U.S. BLM, 2003). CBNG water disposal is a major concern from several points of view (Rice et al., 2000), including landowners worried about future land use and the availability of water.

The use of CBNG water to enhance cropland and rangeland forage production would allow for recharging of the groundwater system; however, much of the CBNG water currently being produced in the PRB does not meet irrigation water quality standards (Bartos and Ogle, 2002). In addition, nearly 41% of the PRB consists of soils characterized as having poor drainage (U.S. BLM, 2003). CBNG waters are typically high in sodium (Na⁺) and bicarbonate (HCO₃⁻) and there is evidence land application could cause soil salinity and sodicity problems (Rice et al., 2000). The objective of this work was to better understand the chemical interactions taking place between treatment combinations of CBNG water and the semi-arid soils of the PRB with cropland irrigation.

Excessive levels of salts impact large areas of soils around the world. The primary impacts of salts on soil quality are associated with saline and sodic conditions. Saline soil conditions are associated with excess salts such as chlorides (Cl⁻) and sulfates ($SO_4^{2^-}$) of Na⁺, calcium (Ca²⁺), and magnesium (Mg²⁺) (Sumner et al., 1998). In semi-arid soils, carbonate ($CO_3^{2^-}$) is usually the dominate anion in solution. Problems associated with salinity and sodicity are related to the ability of plants to uptake water to facilitate photosynthesis. As the salinity of the soil increases, plants, depending on their level of salt tolerance, become less able to absorb the amounts of water needed for optimal biomass production due to reduced osmotic potential by the plant root (Bauder and Brock, 2001). Increased sodicity is associated with the degradation of soil structure and infiltration, and hydraulic conductivity. The major effect of sodicity on soils is associated with soil structure. Elevated levels of Na⁺ promote aggregate slaking and clay particle dispersion, thus affecting the flow of oxygen, water, and nutrients to the plant root system resulting in decreased plant productivity, lower microbial biomass, and the destruction of once-productive soils.

A sodic soil is defined as a soil that has been adversely impacted physically by the presence of Na^+ adsorbed to cation exchange sites (U.S. Salinity Laboratory Staff, 1954). The effect of Na^+ , as characterized by sodium adsorption ratio (SAR) or exchangeable sodium percentage (ESP), on the physical character of a soil has been shown to be greatly dependent on the salinity of the soil. It would be difficult to estimate the impact of high or low SAR values on the physical state of a soil without evaluating the EC of the system (Shanmuganathan and Oades, 1983). Any attempt to set critical SAR or ESP values for land management would be arbitrary unless EC is also taken into consideration simultaneously with Na⁺ concentration (Sumner et al., 1998). Research has shown that elevated SAR values do not cause physical degradation if soils are coarse textured or if the system contains high levels of soluble salts. This was first demonstrated by Quirk and Schofield (1955). Their work demonstrated that soil materials with an ESP of 40 maintained a stable permeability with an electrolyte concentration of about 30 mmol L⁻¹ (EC ≈ 2.1 dS/m). McNeal and Coleman (1966) found that typical arid land soils having clay mineralogy dominated by 2:1 layer silicates, but only moderate amounts of montmorillonite, can tolerate ESP values of 15 or greater before serious reductions in hydraulic conductivity occur, if the salt concentration of the solution exceeds 3 mmol L⁻¹. Gardner et al. (1959) came to the same conclusion dealing with unsaturated soils.

The impact of sodicity on the physical properties of soils is dependent on the EC associated with the system. For example, if salt is added to a dispersed clay suspension, the increased EC of the suspension will cause the clay particles to flocculate. The minimum EC required to cause flocculation is referred to as the threshold electrolyte concentration (TEC) or flocculation value (FV) and has been discussed by Quirk and Schofield (1955), Sumner et al. (1998), and Chaudhari and Somawanshi (2004). This value is dependent on counter-ion valency, pH, clay type, and texture. If salinity is maintained at or above the TEC value for a specific material, the physical condition of the material will be maintained in a flocculated state, no matter how high the SAR (Sumner et al., 1998). However, if the salinity level is low, a highly sodic soil will slake and disperse and soil structure will deteriorate. The TEC values for Na montmorillonite were shown to be about 12 mmol L^{-1} NaCl and 0.25 mmol L^{-1} CaCl₂ for Ca montmorillonite (Van Olphen, 1977). Corresponding TEC values for Na and Ca illites were found to be 40 mmol L^{-1} to 50 mmol L^{-1} NaCl and 0.25 mmol L^{-1} CaCl₂, respectively (Arora and Coleman, 1979). Sposito's 1989 review of the above literature suggested that a fully Na-saturated smectite suspension will flocculate if the electrolyte concentration is $>8.0 \text{ mmol } \text{L}^{-3}$ and a suspension of Na^+ illite will do the same if the electrolyte concentration reaches about 50 mmol L⁻¹. His conclusion was that soil salinity tends to counteract the negative effect of exchangeable Na⁺ on soil structure. The presence of divalent ions such as Ca^{24} would additionally lower the TEC needed to maintain good soil structure.

The application of irrigation water or rainfall to soil materials that have elevated SAR can result in clay dispersion. Irrigation waters generally have low EC values and do not meet the TEC required to maintain soil structure in the presence of exchangeable Na⁺. In addition, mechanical forces resulting from raindrop impact, the flow of water at the surface due to flooding, or the use of farm equipment can enhance clay dispersion; however, if measures are taken to eliminate these potential impacts to the system, a soil with high EC and SAR will maintain good physical structure. One method to eliminate these potential impacts is to treat the soil surface with an amendment such as gypsum (CaSO₄•2H₂O) or sulfur (S). These amendments individually and in combination are currently being used in the PRB for CBNG water application to agricultural croplands and rangelands. Gypsum is used as a surface amendment to increase the level of Ca²⁺ in the system. Increased Ca²⁺ concentrations in solution compete for available cation exchange sites on clay surfaces, resulting in Na⁺ being leached from the system with increased irrigation events. Sulfur is used as a surface amendment to decrease the pH of the system and enhance calcite (CaCO₃) dissolution releasing Ca²⁺ into the soil solution. The oxidation of S, occurring mainly via microbial processes, results in the production of acidity enhancing the dissolution of CaCO₃.

The chemistry associated with saline and sodic conditions in soils is complex. The objective of this work was to better understand the chemical interactions taking place between treatment combinations of CBNG water and the semi-arid soils of the PRB with cropland irrigation. Understanding these interactions may lead to the successful use of CBNG water to improve vegetation production on irrigated croplands.

Materials and Methods

Study Area

The study was conducted on a 15 ha irrigated field near Ucross, Wyoming. Located on the north side of the Piney Creek drainage, the field has historically been cultivated and used for grazing and hay grass production. The field has been flood irrigated for the last 10 years and was planted in an alfalfa/grass mix in 1995.

Initial Field Characterization

CBNG water used for irrigation on the study site was collected from a multiple-well discharge location. Water samples were collected in 20 L containers for laboratory testing. Containers were purged with argon to reduce the incorporation of O_2 into the water during collection. Field parameters tested included temperature, pH, and EC. Samples collected for initial characterization were filtered using 0.45 µm filters and stored under cool conditions until analysis was complete. Water samples were analyzed for EC, total alkalinity, Na⁺, Ca²⁺, Mg²⁺, K⁺, Fe³⁺, SAR, Cl⁻, F⁻, HCO₃⁻, SO₄²⁻, and CO₃²⁻. Speciation was determined using MINTEQ 1.0. A sulfuric acid titration (Loeppert and Suarez, 1996) was used to determine the relationship between pH and HCO₃⁻. This information was used to adjust sulfur burner rates in the field.

Soil pits were excavated to a depth of 120 cm in nine random locations throughout the studyfield and a detailed soil survey was completed to aid in the classification of predominant soil types and suitability for CBNG water application. The slope and aspect at each test-pit was noted, along with the following soil profile characteristics - depth of horizons, texture-by-feel, consistence, structure, effervescence, and percent coarse fragments. Soil samples were collected from random soil profiles and analyzed for the chemical parameters: pH, EC, alkalinity, Na⁺, Ca^{2+} , Mg²⁺, Cl⁻, SO₄²⁻ (Helmke and Sparks, 1996; Frankenberger et al., 1996; Tabatabai, 1996) and textural class based on percent sand, silt, and clay (Gee and Or, 2002).

Three soil mapping units were identified in the study site and included Forkwood silty clay loam, Ulm silty clay loam, and Kishona loam. Forkwood silty clay loam is the predominant map unit representing 83% (12.6 ha) of the study site, Ulm and Kishona soils comprised 12% (1.8 ha) and 5% (0.8 ha) of the remaining area. The Ulm mapping unit represented the greatest limitations because of elevated clay content; surface horizon clay content ranged from 28 to 50%, indicating potential low infiltration and permeability. Clay content of the Forkwood and Kishona soils ranged from 20 to 35%. These soils are structurally more stable and past cultivation of this site may further enhance surface conditions. Soil pit sites and estimated soil mapping unit locations are shown in Fig. 1.

Study Area and Sample Plot Establishment

Study areas were established along the side of the irrigation risers (water sources for side roll irrigator) indicated by the dots in Fig. 1. A total of 18, 15 x 24 m study areas were established in the study field (Fig. 1). These study areas were located 15 m west and 1.5 m south of risers, then divided into eight, 6 x 6 m square study plots. Four study plots were located at the top and four at the bottom of each study area with a 3 m buffer down the middle.

Baseline Characterization

Soil samples were randomly collected within each study plot to verify homogeneity and for baseline characterization. Sample location was determined by randomly selecting a separate length along the X and Y axis of each plot Soil samples were collected based on horizonation, with the top three horizons being sampled. Soil samples from each horizon were homogenized and saturated pastes were prepared using the method described by Rhoades (1996). Chemical analysis of paste extract solutions included pH, EC, alkalinity, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻. Baseline data were analyzed statistically to determine variation between treatment plots prior to treatment application.



Figure 1 Soil pit locations and soil mapping unit (FW-Forkwood, KA-Kishona) locations. Row of dots running north and south represent riser locations. Study areas are represented with rectangles.

Soil Amendments and Water Treatments

Soil amendment and water treatment combinations were used to adjust the soil/water conditions to allow for irrigation with highly sodic CBNG water. Treatments evaluated at the site included combinations of irrigation waters, soil amendments, and water treatments, as shown in Table 1.

Soil amendments were applied to plots after baseline analyses were completed. Soil amendments included agricultural grade sulfur (90% sulfur and 10% bentonite) at a rate of 1.1 Mg ha⁻¹, rock gypsum (87% gypsum) at a rate of 3.4 Mg ha⁻¹, sulfur at a rate of 1.1 Mg ha⁻¹ plus gypsum at a rate of 3.4 Mg ha⁻¹, and no treatment. Mathematical adjustments were made for the purity of the gypsum and sulfur to ensure appropriate application rates. Rock gypsum was sieved to a mesh size of 0.32 cm. Gypsum and sulfur were applied using a drop spreader to ensure even distribution. Soil amendments were initially applied during the first irrigation season (2003); however, due to availability of CBNG water, only one irrigation cycle using Piney Creek water was completed over the entire field. In addition, the PC/CBNG irrigation water treatment was tested to ensure proper operation and control of PC/CBNG water mixing. This allowed for initial reaction and dissolution of soil amendments. Soil amendments were reapplied at the same rates prior to the spring (2004) irrigation season.

Water Used	Surface Applied Soil Treatment	Water Treatment Before Irrigation	Abbreviations Used
Piney Creek (PC)	none	none	PC+NT
PC	gypsum	none	PC+G
PC	sulfur	none	PC+S
PC	Gypsum & sulfur	none	PC+GS
CBNG	none	none	CBNG+NT
CBNG	gypsum	none	CBNG+G
CBNG	sulfur	none	CBNG+S
CBNG	Gypsum & sulfur	none	CBNG+GS
CBNG	none	gypsum injector	CBNG-G+NT
CBNG	gypsum	gypsum injector	CBNG-G+G
CBNG	sulfur	gypsum injector	CBNG-G+S
CBNG	Gypsum & sulfur	gypsum injector	CBNG-G+GS
CBNG	none	gypsum inj. & sulfur burner	CBNG-GSB+NT
CBNG	gypsum	gypsum inj. & sulfur burner	CBNG-GSB+G
CBNG	sulfur	gypsum inj. & sulfur burner	CBNG-GSB+S
CBNG	Gypsum & sulfur	gypsum inj. & sulfur burner	CBNG-GSB+GS
PC/CBNG blend	none	none	PC/CBNG+NT
PC/CBNG blend	gypsum	none	PC/CBNG+G
PC/CBNG blend	sulfur	none	PC/CBNG+S
PC/CBNG blend	Gypsum & sulfur	none	PC/CBNG+GS

Table 1. Irrigation water treatments and surface amendments combinations.

CBNG water treatments included acidification and HCO_3^- removal via SO_2 addition with a sulfur burner, solution grade gypsum via a gypsum fertigation applicator, no treatment, and blending with Piney Creek water. Piney Creek water was used as the control. Surface amendment and water treatment requirements were calculated so that sufficient Ca^{2+} was added

to CBNG water and/or soil to obtain a final SAR of approximately 8.0 mmol^{1/2} L^{-1/2}. Using the acid titration method previously described, reduction of CBNG pH to 6.5 removed HCO₃⁻ to levels that resulted in under-saturation of CaCO₃. There was a concern that the sulfur burner would not be able to deliver enough acidity by adding SO₂ to drop the pH lower than 6.5. CBNG water was passed through the sulfur burner and the treated water was oxygenated to facilitate the oxidation of SO₂ to SO₄²⁻ resulting in acidification. Oxidation occurred while pumping the CBNG treated water into holding tanks where the water was stored until being applied. Solution grade gypsum was injected into the CBNG water at two rates to achieve a final SAR of the CBNG water of 8.0 mmol^{1/2} L^{-1/2}. Injection rates were calculated based on SAR values adjusted for CO₃²⁻ and HCO₃⁻ concentrations. Solution grade gypsum was injected at a rate of 0.75 g L⁻¹ for water not treated with the sulfur burner, and a rate of 0.72 g L⁻¹ for water treated with the sulfur burner.

Statistical Approach

A split-plot in space and time experimental design was selected for the study area. This design allowed for analysis of effects of different water types and soil treatments on soil chemistry and their interactions. Statistics were run on mean values for pre and post irrigation data and comparisons between horizons and surface amendments. Analyses were performed using the GENSTAT 4.1 statistical software. The model consisted of water quality as the mainplot effect, soil treatments as sub effect, and soil horizons as sub-sub effect. Water quality was a random effect, and all other components were fixed. Differences among treatment means were tested using Fisher's Least Significant Difference Test (LSD) at $P \le 0.05$ (Steel and Torrie, 1980).

Results and Discussion

Irrigation Water Characterization

Two irrigation waters were used in this study. Piney Creek (historic source of irrigation water) was used as the control and CBNG water from a common wellhead on the property. Table 2 shows the water chemistry for both waters.

Water	pН	EC	TDS	ALK	Na^+	Ca ²⁺	Mg^{2+}	SAR
Sample	s.u.	dS/m	mg/L	mg/L	mg/L	mg/L	mg/L	$mmol^{1/2} L^{-1/2}$
Piney Creek	8.3	0.64	470	207	28.1	74.8	29.5	0.69
CBNG	8.3	1.38	910	802	344	8.90	3.90	24.3
	\mathbf{K}^+	Fe	но	CO3 ⁻	Cl ⁻	\mathbf{F}^{-}	CO_{3}^{2}	SO ₄ ²⁻
	mg/L	mg/L	m	g/L	mg/L	mg/L	mg/L	mg/L
Piney Creek	5.8	100	2	37	2.5	0.19	7.5	137
CBNG	3.1	560	8	53	12.8	0.94	61.5	<1.0

Table 2. Water chemistry for Piney Creek and CBNG waters used at the study site.

Irrigation water was applied using a side-roll irrigation system. The side-roll was placed perpendicular to study plots. Sprinkler nozzles were 12 m apart and set to deliver 25 L min⁻¹. Plots were irrigated in two, 11 hour intervals. Four irrigation events (1 event = one 11 hour interval at all risers) were completed during the irrigation season. A total of 31 cm of water was applied to each study area. The same irrigation treatment was used for the risers above and below each study area.

Gypsum and sulfur soil amendments were applied and the water treatment systems and sideroll irrigation system were installed. However, due to the lack of available CBNG water in 2003, only a brief testing of the irrigation system occurred before irrigation was terminated due to winter weather conditions. Approximately 8 cm of Piney Creek water was applied to the entire site during this initial testing period. In addition, the PC/CBNG irrigation water treatment was tested on the PC/CBNG plot area to ensure proper operation and control of PC/CBNG water mixing.

Piney Creek water represents typical irrigation water for the region. Calcium and HCO_3^- are the most active ions in solution. This is expected for a semi-arid region with alkaline dominated soils. Results using the MINTEQ model indicate $CaCO_3$ is the controlling mineral for Ca^+ and HCO_3^- in the system. Application of Piney Creek water for irrigation is not expected to cause any problems with soil structure and associated hydraulic conductivity.

Sodium, and HCO_3^- are the dominant cation and anion in the CBNG water. As discussed previously, Na⁺ is the most problematic ion when dealing with CBNG water and its potential use for irrigation. With a SAR value of 24.3 mmol^{1/2} L^{-1/2}, the EC of 1.38 dS m⁻¹ is not high enough to meet the TEC required to maintain soil structure. However, the use of soil amendments is expected to increase the EC to a level high enough to meet TEC requirements. The dissolution of CaSO₄ will directly increase the EC of the soil solution, while addition of S and its subsequent acidification upon oxidation will result in the dissolution of CaCO₃, in turn increasing the EC of the soil solution (Mace et al., 1999). Results using the MINTEQ model indicate the CBNG water is supersaturated with respect to HCO₃⁻. The application of CBNG water to the soil surface is expected to result in the precipitation of CaCO₃. Acidification of the CBNG water via the sulfur burner and the subsequent reduction in HCO₃⁻ will help maintain Ca⁺ levels in solution.

Field Studies

In spring 2004, soil samples were collected from each plot prior to irrigation treatment for chemical analysis. Calcium and SO_4^{2-} levels increased on all G, S, and GS amended plots with a slight increase in Na⁺ on the PC/CBNG irrigation treatment plots. These results were not directly included in the statistical analysis.

Soil saturated paste extracts indicated very few differences in pH between pre and post irrigation for all water treatments except CBNG and CBNG-GSB (Table 3). Plots receiving CBNG water treatment had significant decreases in pH irrespective of soil surface amendments. The CBNG+S does not prove to significantly affect the pH in the A horizon; however, with a P=0.058 it is close. Decreases in pH are associated with the addition of $SO_4^{2^-}$ to the system and subsequent acidification reactions. It is unclear why $SO_4^{2^-}$ additions had this affect with the CBNG and CBNG-GSB water treatments and not the PC, CBNG-G, or PC/CBNG water treatments. There were no significant differences between PC/CBNG and PC plots at any depth. The lack of differences is attributed to the lower number of replications (e.g., only 2). In addition, the pH values seem to increase for the PC/CBNG, which can not be explained at this time.

Increases in EC were observed for all amendments and soil horizons excluding the NT and PC/CBNG plots (Table 4). Increased EC in the Bt_2 horizon indicated that irrigation water percolated into the Bt_2 . Increased EC resulted from soil mineral dissolution, dissolution of soil amendments, CBNG water treatments of CaSO₄ and S, and/or soluble ions in CBNG water.

	Water	Soil]	Pre Irr	igation		Post Irrigation				
Variable						Soil '	Treatme	ent			
	Treatment	Horizon	NT	G	S	GS	NT	G	S	GS	
рН	PC	А	7.25	7.38	7.38	7.33	7.76 ^A	6.80 ^{Bb}	7.34 ^{AB}	7.28 ^{AB}	
		Bt_1	7.65	7.63	7.70	7.58	7.79	7.72 ^a	7.773	6.95	
		Bt_2	7.78	7.90	7.85	7.75	7.76	7.67 ^a	7.405	7.41	
	CBNG	А	7.45	7.35	7.33	7.40	7.13	7.15	7.10	7.00	
		Bt_1	7.63	7.65	7.68	7.75	7.13	7.05	7.13	7.08	
		Bt_2	7.80	7.88	7.88	7.90	7.18	7.10	7.20	7.41	
	CBNG-G	А	7.50	7.43	7.43	7.50	7.03 ^B	7.39 ^{AB}	7.90 ^A	7.46 ^{AB}	
		Bt_1	7.68	7.73	7.70	7.65	7.45	7.51	7.90	7.85	
		Bt_2	7.88	7.83	7.85	7.83	7.13	7.56	7.77	7.76	
	CBNG-GSB	А	7.03	7.20	7.08	7.20	7.03	6.88	6.98	6.93	
		Bt_1	7.35	7.53	7.40	7.45	7.03	6.98	7.49	7.08	
		Bt_2	7.63	7.65	7.55	7.65	7.15	7.10	7.49	7.10	
	PC/CBNG	А	7.16	7.26	7.21	7.31	8.88 ^A	7.84 ^B	7.80 ^B	6.91 ^{Cb}	
		Bt_1	7.56	7.46	7.56	7.51	8.79 ^A	7.35 ^B	6.96 ^B	8.72^{Aa}	
		Bt ₂	7.76	7.76	7.76	7.61	8.71 ^A	7.75 ^{AB}	7.06 ^B	8.55 ^{Aa}	

Table 3. Mean pH values for soil saturated paste extracts of pre and post Piney Creek and CBNG irrigation treatment sites receiving water and soil amendments. Abbreviations are described in Table 1. Post irrigation treatment LSD = 0.85

BOLD – Significant differences between means of pre irrigation and post irrigation samples at same depth ($P \leq 0.05$).

Capital letters indicate a significant difference between means of amendments (P≤0.05).

Lower case letters indicate a significant difference between means of soil horizons (P≤0.05).

Increases in EC have been shown to reduce the negative effects of Na⁺ on the physical degradation of a soil (Shanmuganathan and Oades, 1983, Van Olphen, 1977, Arora and Coleman, 1979, Sumner et al., 1998). Increases in EC help to meet the TEC requirement for maintaining good soil structure at a given SAR. However, EC must be maintained below plant tolerance levels. Increases in EC may affect the crop selectivity for the site and should be monitored to prevent salinization. Current EC values are within tolerance levels for most wheatgrass and clover species. Alfalfa shows the lowest tolerance for CBNG water irrigation with a threshold value of 2.0 dS m⁻¹ (Kotuby-Amacher et al., 2000).

The diffuse double layer has also been shown to be very important in maintaining soil structure (Abu-Sharar et al., 1987, Rengasamy and Olsson, 1991, Rengasamy and Sumner, 1998). In the past, soil scientists have used a model involving the electrical diffuse double-layer theory to explain sodic soil behavior. In natural systems, complex clay systems are bound together into aggregates with silt and sand particles by inorganic and organic compounds. Rengasamy and Sumner (1998) have developed a model describing the processes that take place during the wetting of a dry soil aggregate. Their model describes the influences of salinity and sodicity on the physical nature of natural soil systems. As dry aggregates are wetted, hydration forces become important. The stability of aggregates, and hence the pore systems, depends on attractive and repulsive forces resulting from intermolecular and electrostatic interactions

between the soil solution and soil particles (Rengasamy and Olsson, 1991). In general, if clay particles are saturated with Ca^{2+} or Mg^{2+} , aggregates are held together by these cations. If the clays are saturated by monovalent cations such as Na⁺, the clay particles may be separated depending on the ionic strength, e.g., EC. The result is clay dispersion. An increase in EC produced by an increase in Ca^{2+} due to amendments and water treatments will decrease the effect of Na⁺, maintaining soil structure.

			\mathcal{O}										
				Pre Irı	rigatior	ı	Post Irrigation						
Variable	Water	Soil	Soil Treatment										
	Treatment	Horizon	NT	G	S	GS	NT	G	S	GS			
EC	PC	А	0.885	0.890	0.893	0.840	0.943 ^B	1.50 ^{AB}	1.49 ^{ABb}	2.06 ^A			
dS m ⁻¹		Bt_1	0.608	0.610	0.623	0.608	0.806	1.417	1.00^b	1.56			
		Bt_2	0.575	0.550	0.560	0.547	0.755 ^C	2.08 ^B	2.99 ^{Aa}	2.07 ^B			
	CBNG	А	0.830	1.21	1.07	0.980	1.52 ^B	2.08 ^{AB}	2.43 ^{Aa}	2.84 ^{Aa}			
		Bt_1	0.625	0.763	0.610	0.535	0.800 ^B	1.91 ^A	1.23 ^{ABb}	1.94 ^{Ab}			
		Bt ₂	0.580	0.588	0.543	0.505	0.730 ^B	2.02 ^A	1.12 ^{Bb}	2.03 ^{Aab}			
	CBNG-G	А	0.728	0.800	0.833	0.873	1.78	2.47	2.39	2.52			
		Bt_1	0.528	0.545	0.550	0.628	1.32	1.84	1.55	1.92			
		Bt_2	0.498	0.515	0.510	0.550	1.02 ^B	2.21 ^A	1.75 ^{AB}	2.24 ^A			
	CBNG-GSB	А	1.04	0.863	0.933	0.893	1.99 ^B	3.90 ^{Aa}	3.12 ^{Aa}	3.72 ^{Aa}			
		Bt_1	0.513	0.430	0.575	0.603	1.76 ^C	3.28 ^{Aab}	2.11 ^{BCb}	2.63 ^{ABb}			
		Bt ₂	0.503	0.488	0.528	0.470	1.75	2.57 ^b	2.07 ^b	2.54 ^b			
	PC/CBNG	А	1.11	1.11	1.07	0.820	1.31	1.47 ^{ab}	1.56	1.83 ^a			
		Bt_1	1.00	1.32	0.82	0.660	1.22	1.18 ^b	0.854	0.923 ^b			
		Bt ₂	1.75	1.57	1.05	1.19	0.973 ^B	2.10 ^{Aa}	1.03 ^B	1.48 ^{ABab}			

Table 4. Mean EC values for soil saturated paste extracts of pre and post Piney Creek and CBNG irrigation treatment sites receiving water and soil amendments. Abbreviations are described in Table 1. Post irrigation treatment LSD = 0.884.

BOLD – Significant differences between means of pre irrigation and post irrigation samples at same depth (P≤0.05).

Capital letters indicate a significant difference between means of amendments ($P \leq 0.05$).

Lower case letters indicate a significant difference between means of soil horizons ($P \leq 0.05$).

Post irrigation soil chemistry data show a significant increase in SAR in the A and Bt₁ horizons in all plots irrigated with CBNG water (Table 5). The highest SAR (7.74 mmol^{1/2} L^{-1/2}) occurred in the CBNG+NT treatment with an increased from 0.45 to 7.29 mmol^{1/2} L^{-1/2}. This was expected due to no amendment or treatment of the CBNG water. Plots with surface treatments (CBNG+GS, CBNG+G, and CBNG+S) were significantly lower than CBNG+NT with the CBNG+GS having the lowest SAR value of 4.49 mmol^{1/2} L^{-1/2}. The difference between the CBNG+GS plot and the CBNG+G and CBNG+S plots can be attributed to the lower overall amount of amendment application and slow conversion rate of elemental S to SO₄²⁻ by soil microorganisms. There were no significant differences in SAR in the Bt₁ horizon with amendments.

Table 5. Mean SAR values for soil saturated paste extracts of pre and post Piney Creek and CBNG irrigation treatment sites receiving water and soil amendments. Abbreviations are described in Table 1. Post irrigation treatment LSD = 1.16.

	Water	Soil		Pre Irr	rigation		Post Irrigation				
Variable						Soil T	reatmen	nt			
_	Treatment	Horizon	NT	G	S	GS	NT	G	S	GS	
SAR	PC	А	0.347	0.300	0.330	0.374	0.768	0.536	0.557	0.470	
$mmol^{1/2} L^{-1/2}$		Bt_1	0.650	0.537	0.549	0.512	0.734	0.522	0.633	0.596	
		Bt ₂	0.617	0.563	0.535	0.430	0.846	0.620	0.672	0.563	
	CBNG	А	0.452	0.262	0.255	0.301	7.74 ^{Aa}	5.64 ^{Ba}	6.06 ^{Ba}	4.49 ^{Ca}	
		Bt_1	0.628	0.475	0.528	0.528	2.29 ^b	2.04 ^b	2.67 ^b	2.40^b	
		Bt ₂	0.638	0.583	0.580	0.579	1.25 ^b	0.942 ^b	1.09 ^c	0.924 ^c	
	CBNG-G	А	0.382	0.280	0.336	0.376	7.50 ^{Aa}	5.56 ^{Ba}	5.69 ^{Ba}	4.97 ^{Ba}	
		Bt_1	0.597	0.492	0.556	0.516	2.93 ^b	3.19 ^b	2.72 ^b	2.77 ^b	
		Bt ₂	0.648	0.648	0.662	0.631	1.04 ^c	0.966 ^c	0.865 ^c	0.998 ^c	
	CBNG-GSB	А	0.363	0.388	0.318	0.317	5.54 ^{Aa}	3.67 ^{Ba}	4.38 ^{Ba}	3.91 ^{Ba}	
		Bt_1	0.421	0.560	0.581	0.581	2.68 ^b	2.68 ^b	3.66 ^a	3.41 ^a	
		Bt ₂	0.553	0.708	0.605	0.745	1.06 ^c	1.08 ^c	1.20 ^b	1.18 ^b	
	PC/CBNG	А	0.217	0.183	0.210	0.241	3.77 ^a	3.45 ^a	3.68 ^a	4.34 ^a	
		Bt_1	0.721	0.509	0.537	0.531	1.67 ^b	1.83 ^b	1.92 ^b	1.43 ^b	
		Bt ₂	1.58	3.10	2.57	1.69	1.46 ^b	1.66 ^b	1.67 ^b	0.798 ^b	

BOLD – Significant differences between means of pre irrigation and post irrigation samples at same depth (P≤0.05).

Capital letters indicate a significant difference between means of amendments ($P \leq 0.05$).

Lower case letters indicate a significant difference between means of soil horizons ($P \leq 0.05$).

The CBNG-G water treatment follows a similar trend as the CBNG treatment in the A and Bt₁ horizons with respect to SAR (Table 5). Again, the CBNG-G+NT had the highest SAR (7.70 mmol^{1/2} L^{-1/2}) in the A horizon and was significantly greater than the CBNG-G+GS, CBNG-G+G, and the CBNG-G+S amendments. Interestingly, the CBNG-G+NT resulted in a greater change in SAR (7.12 mmol^{1/2} L^{-1/2}) than all CBNG with soil amendment plots. The addition of CaSO₄ to the irrigation water was expected to result in greater availability of Ca²⁺ and more rapid leaching of Na⁺ through the soil profile. There were no significant differences in SAR in the Bt₁ horizon with soil amendments.

SAR values in the CBNG-GSB water treatment again follow the same trend as the CBNG and CBNG-G water treatments with significant increases in SAR in the A and Bt₁ horizons (Table 5). The CBNG-GSB+NT showed the highest SAR (5.54 mmol^{1/2}L^{-1/2}) in the A horizon and was significantly greater than the CBNG-GSB+GS, CBNG-GSB+G, and CBNG-GSB+S amendments. Increases in SAR were observed for all treatments in the Bt₁ horizon; however, no significant differences were observed between soil amendments. In addition, significant increases in SAR were observed in the Bt₂ horizon for CBNG-GSB+NT and CBNG-GSB+S. It appears the Na⁺ is moving into the Bt₂ horizon at a greater rate in the CBNG-GSB+NT and

CBNG-GSB+S plots than the CBNG-GSB+GS and CBNG-GSB+G plots, however; there is no significant difference between the soil amendments in the Bt₂ horizon.

Results also indicated a significantly higher concentration of SO_4^{2-} in treatments where gypsum and SO_2 are added to the irrigation water (Table 6). Sulfate is expected to be readily mobile, in part due to the fact that it does not interact, to any large degree, with the cation exchange reactions in the soil. This is confirmed by the increased concentrations of SO_4^{2-} in the Bt₂ horizon. Surface applied S is delayed in its activity and reaction with the soil because it is dependant on microbial transformation and oxidation to be converted from elemental S to SO_4^{2-} . This conversion occurs at a slower rate and is an important reason why S amendments lag behind SO_4^{2-} added to irrigation water. Mace et al. (1999) and Prather et al. (1978) showed that addition of sulfuric acid (H₂SO₄), in the presence of CaCO₃, is more effective in sodic soil reclamation than CaSO₄. Mace et al. (1999) found that the addition of H₂SO₄ resulted in the soil being supersaturated with respect to CaSO₄. Sulfuric acid has also been shown to improve infiltration rates and soil structure primarily due to an increase in EC from CaCO₃ dissolution, and solubilization of Al- and Fe-hydroxyl compounds that can promote flocculation and stabilization of soil structure (Prather et al., 1978).

Table 6. Mean SO_4^{2-} concentrations for soil saturated paste extracts of pre and post Piney Creek and CBNG irrigation treatments sites receiving water and soil amendments. Abbreviations are described in Table 1. Post irrigation treatment LSD = 8.08.

			Pre Irrigation			Post Irrigation					
Variable	Water	Soil				Soil 7	[reatm	ent			
	Treatment	Horizon	NT	G	S	GS	NT	G	S	GS	
SO4 ²⁻	PC	А	0.600	0.450	0.375	0.400	1.75 ^C	12.1 ^{Bb}	11.0 ^B	20.2 ^A	
$mg L^{-1}$		Bt_1	0.875	0.675	0.725	0.600	2.7 ^B	12.7 ^{Ab}	6.13 ^{AB}	15.1 ^A	
		Bt_2	1.125	1.025	1.20	0.717	3.85 ^B	22.5 ^{Aa}	8.17 ^B	22.2 ^A	
	CBNG	А	0.425	0.625	0.525	0.525	2.27 ^C	11.2 ^{Bb}	18.4 ^{ABa}	24.9 ^A	
		Bt_1	0.500	0.700	0.825	0.525	2.04 ^B	18.6 ^{Aab}	6.51 ^{Bb}	18.5 ^A	
		Bt_2	0.850	0.750	1.050	0.775	3.98 ^B	21.8 ^{Aa}	9.40 ^{Bb}	22.9 ^A	
	CBNG-G	А	0.450	0.475	0.450	0.525	3.96 ^B	14.4 ^A	14.9 ^A	16.5 ^A	
		Bt_1	0.475	0.600	0.475	0.500	6.03 ^B	13.8 ^{AB}	10.3 ^{AB}	15.7 ^A	
		Bt_2	0.850	0.850	0.650	0.775	7.53 ^B	21.8 ^A	14.7 ^B	22.8 ^A	
	CBNG-GSB	А	0.475	0.500	0.475	0.475	12.8 ^C	38.4 ^{Aa}	27.1 ^{Ba}	37.4 ^{Aa}	
		\mathbf{Bt}_1	0.500	0.300	0.500	0.375	13.6 ^B	32.8 ^{Aab}	17.1 ^{Bb}	25.3 ^{Ab}	
		Bt_2	0.800	0.625	0.700	0.625	16.4 ^B	28.3 ^{Ab}	20.3 ^{ABab}	26.7 ^{Ab}	
	PC/CBNG	А	0.655	0.756	0.705	0.555	1.20 ^B	7.5^{ABb}	6.76 ^{AB}	11.1 ^{Aab}	
		Bt_1	1.21	1.86	2.36	0.955	7.29	10.07^{ab}	3.55	4.53 ^b	
		Bt ₂	2.90	3.80	7.86	3.81	5.27 ^B	18.6 ^{Aa}	6.35 ^B	12.9 ^{ABa}	

BOLD – Significant differences between means of pre irrigation and post irrigation samples at same depth (P≤0.05).

Capital letters indicate a significant difference between means of amendments (P≤0.05).

Lower case letters indicate a significant difference between means of soil horizons (P≤0.05).

Prather et al. (1978) concluded that the combination of H_2SO_4 and $CaSO_4$ "appreciably improved the time and water efficiency as compared to $CaSO_4$ alone" when trying to reclaim a sodic soil. Results from our study showed similar trends for the different amendments. Sulfate concentrations were used as an indication of acidity for each treatment. Most of the acidity produced via water treatment or amendment is expected to be consumed in the surface horizon. Plots with $CaSO_4$ or $CaSO_4$ and S amendments (Table 6) had greater SO_4^{2-} concentrations in the Bt₁ and Bt₂ horizons as compared to the S and NT plots with all water treatments with the exception of the CBNG-GSB+S plot, which is also statistically similar. Moreover, all CBNG-GSB plots resulted in an increase in SO_4^{2-} concentration compared to the other water treatments, indicating the addition of SO_4^{2-} to the irrigation water may be a more effective treatment option to maintain Ca^+ levels the soil system. In addition, SAR values for the CBNG-GSB treatment plots appear to be lower in the surface horizon and higher in the lower horizons as compared to other water treatments indicating an increased leaching rate of Na⁺. Statistics are currently being completed to determine if differences between water treatments are significant.

Since much of the research regarding saline/sodic conditions has been conducted using saturated aqueous systems, some concern also exists for whether these studies apply to unsaturated conditions. Since low water content results in low repulsion forces, unsaturated systems are expected to have higher attractive forces when compared to saturated systems. Rengasamy and Sumner (1998) indicated that spontaneous dispersion takes place when sodic clay is impacted with water of very low electrolyte concentration. However, water content below saturation results in limited swelling and incomplete separation of clay particles, with the distance between particles depending upon the water content. Therefore, aggregate slaking and clay dispersion in unsaturated systems may be limited as compared to saturated systems for specific EC and SAR conditions. Russo and Bresler (1977) demonstrated this fact in their study, which showed that water with a higher SAR can be applied when unsaturated conditions are maintained during irrigation without harming the soil structure, and that the negative effect of high SAR and low EC decreases in unsaturated soils.

The implementation of a leaching fraction after each irrigation season may prove to be a viable treatment method in addition to $CaSO_4$ and/or S. The application of Piney Creek water at the end of the irrigation season would leach Na^+ deeper into the soil profile. Concerns exist when applying a lower EC water to the surface of a soil with increased Na^+ , however, remaining Ca^{2+} and S amendments my increase the EC to a level appropriate for application. More studies are warranted.

Conclusions

Irrigation of croplands at this site with CBNG water resulted in increased EC and SAR in surface horizon saturated paste solutions. However, the use of surface amendments and water treatments resulted in decreased concentrations of Na^+ in surface horizons. With regard to surface amendments only, the GS (gypsum plus S) combination resulted in the lowest SAR in the A horizon, outperforming both the G and S amendments. However, the GS combination did not result in better movement of Na^+ through the profile. No differences were noted between the G and S amended plots, and no differences were found in the Bt₁ and Bt₂ horizons between surface amendments. The addition of CaSO₄ to the CBNG water does not appear to have a significant effect on SAR in the A horizon. SAR values generally were lower in the A horizon and higher in

the Bt_1 horizon indicating a greater rate of leaching of Na^+ , but this cannot be confirmed without additional statistical analysis between treatments which is currently ongoing.

The CBNG-GSB water addition appeared to be the most effective treatment. SAR concentrations with all amendments were lower than both the CBNG and CBNG-G water treatments. In addition, Na⁺ appeared to move through the profile at a greater rate with SAR concentrations being greater in both the Bt₁ and Bt₂ horizons. The removal of HCO₃⁻ from the CBNG water may result in higher soluble Ca²⁺ concentrations that resulted in increased competition for available exchange sites and increased rates of Na⁺ leaching. In addition, SO₄²⁻ lends to the stability of the soil structure by decreasing the pH, increasing the EC, and potentially solubilizing Al- and Fe-hydroxyl compounds that promote flocculation and stabilization of soil structure.

These are preliminary results and more study is needed. These results represent only one irrigation season at one site. A leaching fraction at the end of the irrigation season may prove to be advantageous in moving Na^+ lower in the soil profile.

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