ARTICLE IN PRESS

Applied Geochemistry xxx (2009) xxx–xxx

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Evaluation of amendments used to prevent sodification of irrigated fields

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ARTICLE INFO

Article history:
Received 12 June 2007
Accepted 2 September 2009
Available online xxxx

Editorial handling by Prof. G.M. Filippelli

ABSTRACT

Gypsum and S are applied to soils being irrigated with Na–HCO_3 dominated coalbed natural gas (CBNG) produced water to protect soil structure and fertility. Wyoming law requires beneficial use of produced water and irrigation with CBNG produced water in the semi-arid Powder River Basin is becoming more common. Strontium isotopes were used to evaluate the effectiveness of the gypsum and S applications in preventing sodification of these irrigated soils. The isotope ratio of Sr on the cation exchange complex of irrigated soil falls between that of the gypsum amendment (0.7074) and that of local soil (0.712–0.713). Strontium isotopes indicate that, to a depth of 30 cm, as much as 50% of the Sr on the irrigated soil cation exchange sites originated from the applied gypsum amendment on a field irrigated for 3 a. This was also true to a depth of 5 cm on a field irrigated less than 1 a. Strontium isotope ratio measurements of vegetation illustrate plant utilization of Sr from gypsum amendments, thereby reinforcing the conclusions about the presence of Sr from gypsum on the soil's exchange sites. This Sr tracing technique may be useful in a wide variety of settings where monitoring soil health is necessary, especially in settings where poor quality water is used for irrigation: a more common occurrence as demand for fresh water increases.

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1. Introduction

1.1. Sodic soils

Sodification and salinization of soil is a world-wide problem stemming from cultivation of arid and semi-arid land. Salinization is an accumulation of salt in the rooting zone of the soil profile, while sodification specifically refers to an accumulation of Na on the cation exchange complex of soil. In arid and semi-arid climates, evapotranspiration rates exceed precipitation rates causing concentration of salts in surface soils. Improper irrigation management compounds this problem (Essington, 2004).

The definition of a saline soil is crop specific and ranges from electrical conductivity measurements (in a saturated paste extraction) of $2\ \mathrm{dS\ m^{-1}}$ (or $2\ \mathrm{mS\ cm^{-1}}$) for salt sensitive plants to 8–$10\ \mathrm{dS\ m^{-1}}$ for salt tolerant plants. Excess salt in the soil negatively effects plant growth by limiting plant-available water. Plants use a concentration gradient to force water across membranes; this process becomes less favored as the salinity of soil water increases (Chapin et al., 2002). A soil is considered sodic when the structure of the soil is negatively affected by Na. The larger hydrated radius of Na can cause the soil clay and organic matter to disperse and smectite clays to swell. Dispersion and swelling can reduce macroporosity thereby reducing infiltration capacity and root penetration (Bagarello et al., 2006; Shainberg and Letey, 1984). Additionally, Na is not a plant nutrient and, through displacement of Ca, can cause Ca deficiencies in plants. It is estimated that 10 million hectares of irrigated agricultural land is lost due to salinization or sodification every year. Currently, 23% and 39% of cultivated land is considered saline or sodic, respectively (Essington, 2004; Qadir et al., 2006).

The point at which Na-driven physical changes occur is dependent in part upon soil texture, mineralogy and organic matter content. In general, a soil is defined as sodic when the exchangeable Na percentage (ESP) is over 15; that is, 15% of the base cations on the soil exchange sites are comprised of Na (Essington, 2004; Sumner, 1993; US Salinity Laboratory Staff, 1954). However, several studies have shown that sodic soil conditions, such as reduced infiltration rates and hydraulic conductivities, may occur at ESP values of less than 15 if accompanying levels of salinity are lower than $4\ \mathrm{dS\ m^{-1}}$ (Qadir and Schubert, 2002; Sumner et al., 1998). Therefore, a significant factor determining the extent of the adverse effects of Na^+ on soil properties is the ambient electrolyte concentration in the soil solution, with low concentrations exacerbating the deleterious effects of exchangeable Na.

Prevention or reclamation of sodic soils requires the addition of Ca sources that will prevent or displace Na occupying soil exchange sites. In calcite-rich soils, local Ca can be mobilized through the addition of H_2SO_4, however, additional Ca is often derived from

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doi:10.1016/j.apgeochem.2009.09.001

Please cite this article in press as: Brinck, E., Frost, C. Evaluation of amendments used to prevent sodification of irrigated fields. Appl. Geochem. (2009), doi:10.1016/j.apgeochem.2009.09.001

chemical amendments such as gypsum ($CaSO_4\ 2H_2O$). Gypsum applied to the soil surface helps counteract the negative effects of poor quality (for instance high Na concentration) irrigation water. Gypsum reduces deterioration of smectitic clay-rich soil structure by: (1) increasing the EC of the soil solution thereby compressing the halo of ions (the diffuse double layer) surrounding a charged surface, such as a clay particle and (2) by displacing Na with Ca on the exchange sites (Drever, 1997; Essington, 2004; Qadir et al., 2006; Sumner, 1993). Sodium is then mobile and may be leached below the rooting zone with excess irrigation water. However, application of gypsum has not always been shown to be beneficial in preventing increases in exchangeable Na in irrigated soils (Hulugalle et al., 2006).

1.2. Sodic irrigation water

The suitability of water to be used for irrigation is evaluated, in part, by its Na adsorption ratio (SAR), defined as the ratio of Na to Mg and Ca (units: $\text{mmol}^{1/2}\ \text{L}^{-1/2}$). The specific SAR value that precludes water from use as a source of irrigation depends upon a number of factors including the electrical conductivity (EC) of the water and clay composition of the soil. Generally speaking, however, when the SAR of irrigation water is higher than around 6–12 $\text{mmol}^{1/2}\ \text{L}^{-1/2}$, the Na in the irrigation water can displace Ca from the exchange sites on soil clays and organic matter (Essington, 2004).

In the Powder River Basin, a semi-arid structural and hydraulic basin in northeastern Wyoming and southeastern Montana in the USA (Fig. 1), water coproduced with coalbed natural gas (CBNG) is occasionally used as an irrigation source in this agricultural area. Water associated with CBNG is rich in Na and HCO_3^- with an average SAR value of 14 (standard deviation of 9 measured on 118 samples; Campbell et al., 2008). Powder River Basin CBNG development, like most CBNG production, includes releasing CH_4 by depressurizing a coal seam through dewatering (DeBruin et al., 2004). In 2008, over 10,700 ha m (107×10^9 L) of water was coproduced with CBNG in the Powder River Basin (Wyoming Oil and Gas Conservation Commission, 2009). The Powder River Basin is expected to produce up to 700,000 ha m of co-produced water over the lifetime of the development (DeBruin et al., 2004). Wyoming law requires beneficial use of produced water (Wyoming statute 41-3-101); viable agricultural uses of this semi-arid area include growing hay for livestock or filling of stock-water ponds. Beneficial use of co-produced water is dependent upon water quality and the state regulatory framework, both of which vary greatly throughout the country. Currently, the National Academy of Sciences is compiling information on issues impacting beneficial use of CBNG produced water and how regulatory frameworks impacting beneficial use differ by state. A report summarizing their findings will be released around fall of 2010 (National Academy of Sciences, 2009).

In addition to Na, the high HCO_3^- concentrations in CBNG produced water poses further problems in irrigation water by precipitating with Ca (and to a lesser extent Mg) as $CaCO_3$, further reducing the Ca concentration of the CBNG water and raising the SAR values. Elemental S applied to the soil or added to the

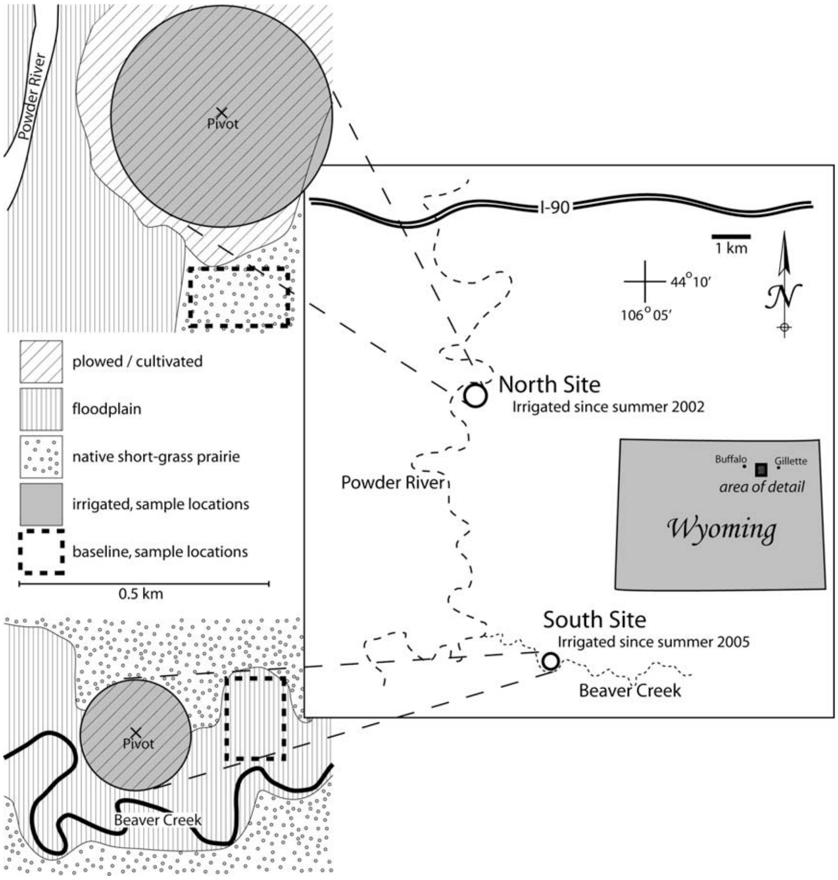

Fig. 1. Map of the study area including locations of the 16 ha (40-acre) pivot North Site and 8 ha (20-acre) pivot South Site. Inset: approximate location of study site within the state of Wyoming. Pull-outs: detail of the irrigated sites including general characteristics. The grey circles represent the area of irrigation; all irrigated samples were taken from within these circles. The dashed line boxes represent the area chosen to represent the baseline, non-irrigated and non-amended soil and vegetation. All baseline samples were taken from these areas.

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irrigation water lowers the pH of the water converting some of the HCO_3^- to CO_2, reducing the precipitation of $CaCO_3$. In general, when using produced water for irrigation, CBNG producers will first discharge the produced water into lined ponds and then pump the water to irrigation systems.

Wyoming is not alone in its increasing use of poor quality irrigation water. Poor quality irrigation water driving salinization and sodification of soils is a growing global concern. As demand for domestic uses of fresh water increases and increasing populations drive the cultivation of less favorable lands, agriculturalists and farmers increasingly turn to saline groundwater or municipal run-off for irrigation water (Hulugalle et al., 2006; Koyro and Lieth, 2008; Wenjun et al., 2008; Yaduvanshi and Swarup, 2005).

1.3. Strontium isotope tracing

Strontium isotopes have been shown to be effective tracers of the Ca cycle (Blum et al., 2000; Capo et al., 1998). The natural variation of Sr isotopes in geologic material is due to the decay of the unstable ^{87}Rb isotope to the stable ^{87}Sr resulting in an $^{87}Sr/^{86}Sr$ value that can fingerprint geologically distinct materials such as commercially mined gypsum from soil. Strontium's chemical similarity to Ca allows it to replace Ca in natural processes and can therefore be used as a natural isotopic tracer of the Ca cycle. The Sr isotopes ^{87}Sr and ^{86}Sr are not fractionated in biogeochemical processes such as evaporation or plant uptake so the $^{87}Sr/^{86}Sr$ ratio will be preserved throughout the soil–plant Ca cycle (Blum et al., 2000).

This study used Sr isotopes to evaluate the effectiveness of gypsum and elemental S in preventing sodification of soils irrigated with Na-rich CBNG co-produced water. The $^{87}Sr/^{86}Sr$ ratio of gypsum was used to trace the fate of introduced Ca from gypsum amendments on CBNG irrigated fields. By identifying the presence of the $^{87}Sr/^{86}Sr$ ratio from gypsum on the cation exchange complex it was possible to calculate the fraction of Sr (and by extension Ca) present upon the exchange sites that originated from applied gypsum. Strontium isotope ratio measurements of vegetation illustrate plant utilization of Sr from gypsum amendments, thereby reinforcing the conclusions about the presence of Sr from gypsum on the soil's exchange sites. Although Sr isotopes have been used to identify its sources of on soil exchange sites (Drouet et al., 2007; Green et al., 2004), this study is the first to quantify the contribution to the cation exchange complex of agricultural soil amendments and thereby assess amendment efficacy.

2. Field sites

This study was carried out on two fields within the Powder River Basin in NE Wyoming that are irrigated with CBNG produced water and receive applications of gypsum and S (Fig. 1). The North Site is a 16 ha (40-acre) irrigated field near the Powder River. The site has undergone intermittent irrigation since the summer of 2002 and has been planted with alfalfa and barley. The South Site is an 8 ha (20-acre) irrigated field near the confluence of Beaver Creek and the Powder River. This site has undergone intermittent irrigation since June of 2005 and is planted with barley. Both fields are irrigated with center-pivot sprinkler irrigation systems.

Application of amendments on the North Irrigated Site included two applications of gypsum (total 14.0 Mg ha^{-1} a^{-1}) in 2005 and one application (4.5 Mg ha^{-1} a^{-1}) in 2006. Sulfur was applied once a year in 2005 (1.2 Mg ha^{-1} a^{-1}) and 2006 (1.4 Mg ha^{-1} a^{-1}). Irrigation water was applied from May to September in 2005 (total 2470 m^3 ha^{-1} or 247 mm) and 2006 (land manager estimates 2500 m^3 ha^{-1}). At the South Irrigated Site, gypsum was applied twice in 2005 (total 10.1 Mg ha^{-1} a^{-1}) and not applied in 2006. Sulfur was applied once in 2005 (2.5 Mg ha^{-1} a^{-1}) and not applied in 2006. Irrigation water was applied June–September in 2005 (total 3220 m^3 ha^{-1}) and May–September in 2006 (510 m^3 ha^{-1}). Exact application rates on the North Site from 2002 through 2004 were unavailable, however the land manager estimates irrigation rates at the North Irrigated Site during the 2002–2004 irrigation seasons (generally May through September) were approximately 6000 m^3 ha^{-1}/a. The first soil and vegetation samples were collected on these fields in August 2005, by which time 700 m^3 ha^{-1} of irrigation water had been applied to the North Site and 1800 m^3 ha^{-1} had been applied to the South Site. Application rates of amendments and water were determined by the land manager based on soil analysis, predicted CBNG water production, economic considerations, and access to amendments.

The evaporation rate in the Powder River Basin has been measured by Payne (2004) to range from 25 to 56 m^3 ha^{-1} day^{-1} (750–1680 m^3 ha^{-1} $month^{-1}$). The irrigation rates at the North and South irrigated sites have varied from 5 to 1775 m^3 ha^{-1} $month^{-1}$, so very little deep infiltration would be expected, especially considering that the measured evaporation rates do not take into account the effect of transpiration.

As a control, undeveloped rangelands adjacent to each irrigated field (dashed boxes in Fig. 1) were chosen for study; hereafter referred to as North Site Baseline and South Site Baseline. The fields are just outside the area of irrigation and amendment application and are therefore considered to represent the baseline for each of the irrigated fields. Vegetation on the baseline fields is native short-grass steppe. Common short-grass steppe species in this part of the Powder River Basin include blue grama (*Bouteloua gracilis*), buffalo grass (*Buchloe dactyloides*), western wheatgrass (*Elymus smithii*), needle-and-thread (*Hesperostipa comata*), and scarlet globemallow (*Spaeralcea coccinea*) (King, 2006). The soil type in this area is Theedle-Shingle-Samday association. These soils are classified as fine-loamy to loamy or clayey-smectitic, mixed, superactive, calcareous, mesic, can be shallow, Ustic Torriorthents (Tarver, 2004). More detailed descriptions of these soils, including particle size distribution, can be found in Ganjegunte et al. (2008) and King (2006).

3. Methods

3.1. Amendments

Samples of the gypsum and S amendments applied to the irrigated fields were collected in July 2005 and April 2006, and a sample of the fertilizer used on the irrigated fields was collected in July 2005. About 0.2 g of the gypsum, S and fertilizer amendments were dissolved in 5 mL of 6 N HCl and an additional 0.2 g of each amendment was dissolved in 5 mL of distilled water. These mixtures were allowed to sit on a hot plate for 72 h. Approximately 1 mL of each solution was dried and re-dissolved in 3.5 N HNO_3. The Sr in the samples was separated using Sr specific resin and analyzed for $^{87}Sr/^{86}Sr$ on a solid source thermal ionization mass spectrometer (TIMS). Concentrations of Sr were determined by isotope dilution using an ^{84}Sr-enriched spike. The internal precision of $^{87}Sr/^{86}Sr$ isotope ratio measurements is ±0.00001. Results of 76 measurements of NBS 987 Sr standard measured during the course of this study had an average $^{87}Sr/^{86}Sr = 0.71026 \pm 0.00002$ (two standard deviations). All analyses were normalized to a $^{86}Sr/^{88}Sr$ ratio value of 0.1194. Analytical blanks were less than 0.002 μg, negligible compared to sample sizes of at least 0.1 μg Sr.

Irrigation water was collected from holding ponds in July 2005, April 2006 and August 2006. Water samples were also collected from the irrigation pivots in August 2006. Water samples were measured for pH and filtered through 0.45 μm sterile filters in the field. A split from each sample was acidified with HNO_3 to

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pH 2 for cation analysis and all samples were kept on ice and in the dark until analysis. The water samples were analyzed for $^{87}Sr/^{86}Sr$ ratios by TIMS and Sr concentration by isotope dilution. Major ion and trace element concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS).

3.2. Soil

Soil samples were collected using a hand auger on each of the four fields (two irrigated, two unirrigated) in August 2005 and in August 2006. In August 2005, on each of the four sites, five random locations were chosen and sampled by depth. The irrigated fields had each been leveled and plowed several times to improve drainage. This resulted in a fairly homogeneous soil system, therefore five samples were deemed sufficient to represent these fields. This sampling regime was chosen to be in accordance with similar studies occurring on the same fields (Ganjegunte et al., 2008; King, 2006). Each sample location was collected in intervals of 0–5 cm, 5–15 cm, and 15–30 cm. In August 2006, one sample location on each field was collected in intervals of 0–5 cm, 5–15 cm, 15–30 cm, 30–60 cm, 60–90 cm, and 90–120 cm. Each soil sample was homogenized and stored in a 0.5 L air-tight plastic bag. Upon returning to the geochemistry laboratory at the University of Wyoming, the water content of the soil was determined by drying 5 g of each soil sample for 48 h at 105 °C. The entire soil sample set was then air dried for 2 weeks and sieved through 2 mm screens.

Cations in soluble salt form and those on cation exchange sites (referred to as extractable cations henceforth) were extracted using the ammonium acetate method (1 M CH_3COONH_4 at pH 7) of Sumner and Miller (1996). This method involves displacing cations on the cation exchange sites with ammonium and measuring the resultant solution (of soluble and exchangeable cations) for major cations and, in this situation, strontium. Concentrations of Na, Ca, Mg, K, Sr were measured by ICP-MS. Cations in only soluble salt form were extracted using the saturated paste method (Rhoades, 1996). In this method, deionized water is added to soil samples until field capacity is reached (shiny but not wet) and allowed to sit for 24 h. The soil water was extracted under vacuum and concentrations of Na, Ca, Mg, K, Sr, Fe, As, Ba, F, Cl, NO_3, PO_4, SO_4 were determined by ICP-MS. Alkalinity was determined through acid titration. In addition, pH and electrical conductivity (EC) were measured on the paste extract. The difference in cation concentrations measured in the ammonium acetate extractions and the saturated paste extractions represents the quantity of cations on the soil's cation exchange sites. Cation exchange capacity (CEC) was measured for each of the samples using the sodium acetate method (1 M NaOAc at pH 8.2) developed by Chapman (1965). Units of CEC are centimoles of charge/kg of soil ($cmol_{(c)}\ kg^{-1}$). Similar to the extractable cation method, Na is first used to saturate the cation exchange sites and is then displaced by NH_4. Sodium concentrations were then determined by atomic adsorption (AA). The two extraction methods were compared to evaluate the CEC measurements. By summing the cations extracted using ammonium acetate – minus the soluble cations – and comparing the results to the $cmol_{(c)}\ kg^{-1}$ measured during the sodium acetate extractions the results were found to be within 1%.

Soil SAR was calculated using the concentrations (in mmol L^{-1}; indicated by square brackets in Eq. (1)) of Na, Mg and Ca from the saturated paste extractions in the definition of SAR from Essington (2004):

$$\mathrm{SAR}\left(\frac{\sqrt{\mathrm{mmol}}}{\sqrt{\mathrm{L}}}\right) = \frac{[\mathrm{Na}^{+}]}{\sqrt{\left[\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right]}} \tag{1}$$

Exchangeable Na percentage (ESP) was calculated using the following equation for ESP (Essington, 2004):

$$\mathrm{ESP} = \frac{[\mathrm{NaX}]}{\mathrm{CEC}} * 100 \tag{2}$$

where [NaX] is the concentration of Na on the soil exchange sites.

The Sr in the ammonium acetate (extractable) and saturated paste (soluble) extractions was isolated through cation chromatography columns and further purified using cation exchange columns filled with Sr specific resin. The resulting Sr separates were analyzed for $^{87}Sr/^{86}Sr$ ratios and Sr concentration by TIMS. The concentration difference between extractable and soluble Sr samples is the amount of Sr on the exchange sites. The $^{87}Sr/^{86}Sr$ ratio for the Sr on the exchange sites was calculated using the isotope mixing equation from Faure (1998):

$$\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}_{\mathrm{Extr.}}} = \frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}_{\mathrm{Exch.}}}(f_{\mathrm{Exch.}}) + \frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}_{\mathrm{Sol.}}}(1 - f_{\mathrm{Exch.}}) \tag{3}$$

The subscripts "Extr", "Exch" and "Sol" stand for Sr isotope ratios of extractable Sr (ammonium acetate extractions), exchangeable Sr and soluble Sr (saturated paste extractions) respectively. The term "$f_{\mathrm{Exch.}}$" represents the fraction of total extractable Sr contributed by exchangeable Sr, where:

$$f_{\mathrm{Exch.}} = \frac{(\mathrm{Sr}_{\mathrm{Extr.}}) - (\mathrm{Sr}_{\mathrm{Sol.}})}{(\mathrm{Sr}_{\mathrm{Extr.}})} \tag{4}$$

and parenthetical terms represent the measured Sr concentrations of the extractable and soluble fractions in mg Sr/kg soil. Strontium isotope ratios and concentrations for extractable and soluble fractions were measured directly; the concentration for exchangeable cations is the difference between these two measured concentrations. These values are used to solve Eq. (3) for the Sr isotope ratio of exchangeable Sr.

Results from Eq. (3), the $^{87}Sr/^{86}Sr$ ratio of exchangeable Sr, were used to calculate the fraction of Sr on the exchange sites that originated from the gypsum. The isotope ratio of the exchangeable Sr on the baseline and irrigated fields, in addition to the Sr isotope ratio of gypsum was substituted into the isotope mixing equation and solved for "f_{Gypsum}" (Faure, 1998):

$$\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}_{\mathrm{Irrigated}}} = \frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}_{\mathrm{Gypsum}}}(f_{\mathrm{Gypsum}}) + \frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}_{\mathrm{Baseline}}}(1 - f_{\mathrm{Gypsum}}) \tag{5}$$

For the irrigated and baseline $^{87}Sr/^{86}Sr$ terms in Eq. (5), values for the average $^{87}Sr/^{86}Sr$ ratio in 2005 samples and the measured value for 2006 samples for each sampled depth interval were used. The $^{87}Sr/^{86}Sr$ ratio used for gypsum is the average of the four measured values: 0.7074. Solving Eq. (5) for "f_{Gypsum}" produces the fraction of Sr on the soil exchange sites that was contributed by gypsum.

Significant differences in soil chemistry and Sr isotope results from the 2005 sampling were determined with two-group *t* tests of means (as described in Phillips, 1982). Variances were evaluated for equality and significance determined at the $p < 0.05$ level (one-tailed). Complete datasets for soil, water and vegetation results are available in Brinck (2007).

3.3. Vegetation

Vegetation samples were collected in August 2005, December 2005, and April 2006. Five random locations were chosen on each of the four fields for each of the three sampling dates. At each sample site a 0.1 m^2 area of vegetation was cut and placed in a 4L plastic bag that was left open to air. Care was taken to avoid including roots and soil in the sample. Samples were allowed to air dry for 2 weeks before being finely ground. Approximately 1 g of the ground vegetation sample was processed following the dry-ashing

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technique in AOAC Official Method 985.01 (Horwitz, 2000). Strontium was separated from the resulting dissolution using Sr specific resin and analyzed for $^{87}Sr/^{86}Sr$ by TIMS. The vegetation was also analyzed for Na, Mg, Ca, Ba, and Sr concentrations using ICP-MS.

4. Results

4.1. Amendments

Strontium isotope ratios were measured for the gypsum, S, fertilizer and irrigation water (Tables 1 and 2). There was no difference between the Sr isotope ratios of amendments digested with water and with HCl, therefore only one ratio is presented for each amendment in Table 1. Very little Sr was detected in the S, fertilizer and irrigation water (Tables 1 and 2). The lowest Sr concentrations were determined in the irrigation water and in the fertilizer, both of which have Sr concentrations <1 mg/L and <1 mg/kg. There is slightly more Sr in the S (3–13 mg/kg) with the higher value found in the HCl digestion. This may indicate that, once oxidized, the S may release more soluble Sr. These low concentrations lead to the conclusion that, at least initially, very little Sr will be contributed to the soil exchange sites by S, fertilizer or irrigation water.

The strontium content of the gypsum was much higher than the other samples analyzed. When dissolved in water, 205 mg/kg Sr was released to solution and when dissolved in HCl, the solution contained 826 mg/kg Sr. The actual amount of Sr contributed/kg gypsum applied will probably be between the two measured concentrations because addition of S to the soil may lower the pH of the soil water. This source of Sr will dominate those contributed by other amendments and irrigation water, and therefore the calculations only account for the Sr contributed by gypsum.

Table 1
Strontium isotope ratio and concentration of soil amendments.

	$^{87}Sr/^{86}Sr$	mg Sr/kg solid	
		H_2O	HCl
Amendments			
Gypsum	0.70742	205	826
Sulfur	0.70816	3.5	13
Fertilizer	0.70879	0.09	0.13

Table 2
Isotope, major ion, and trace element composition of irrigation water (mg/L).

		North site		South site	
		Pond	Pivot	Pond	Pivot
	$^{87}Sr/^{86}Sr$	0.71309	0.71308	0.71206	0.71301
	pH	7.6	8.1	9.2	8.1
	SAR	29	29	21	30
Cations	Na	886	942	2353	965
	Mg	23.0	27.7	631	26.2
	Si	4.9	6.7	1.3	6.6
	K	37.5	39.0	33.0	38.7
	Ca	31.7	35.2	10.9	34.8
	Fe	4.2	3.1	0.6	3.1
Anions	F	2.8	2.9	4.5	3
	Cl	32.8	39.6	3428.3	32.3
	NO_3	8.0	0.2	22.2	0.2
	SO_4	1.2	1.6	551.7	0.4
	Alk (meq/L)	49.2	52.1	57.1	54.2
Trace elements	Li	0.30	0.31	5.78	0.31
	B	0.25	0.27	7.74	0.31
	Al	0.03	0.46	0.01	0.16
	Mn	0.02	0.05	0.01	0.03
	Sr (by ICP-MS)	0.36	0.39	0.08	0.31
	Sr (by TIMS)	0.40	0.30	0.04	0.38
	Ba	0.92	0.96	0.06	1.15
	Br	0.18	0.23	21.80	0.21

Pond samples are averages of samples collected on 8/4/05, 4/21/06 and 8/10/06. Pivot samples were collected on 8/10/06.

The CBNG co-produced waters generally had low concentrations of Ca (11–35 mg/L) as well as low Sr concentrations (0.04–0.40 mg/L) (Table 2) suggesting irrigation water Ca will not be a significant contributor to the exchangeable Ca pool. The Sr isotope ratios (Table 2) do not vary greatly between the pond and pivot samples at the North Site; however the Sr isotope ratio of produced water measured in the retention pond at the South Site was different from the water discharged from the irrigation pivot (0.712 and 0.713, respectively). Additionally, the Sr concentration is greater in water collected from the pivot as opposed to the pond (0.38 versus 0.04 mg/L). At the South Site, the pivot may be delivering a mixture of more than one water source causing it to have a different Sr isotope ratio and major ion composition (Table 2) than the samples taken from the CBNG produced water holding pond. The high SO_4 concentration (550 mg/L) in the South Site pond is not consistent with CBNG co-produced water, which is almost entirely depleted of SO_4. High SO_4 concentrations are not found in the water delivered by the South Site pivot or in the North Site pond and pivot. The SO_4 concentration in the South Site pond may be due to gypsum treatment in the pond water intended to increase Ca concentration in the water which decreases Ba concentrations through precipitation of $BaSO_4$.

4.2. Soil

The North and South irrigated sites have higher SAR, ESP and EC values than baseline in 2005 and shallow 2006 baseline samples (Fig. 2). Average SAR values range from 9 to 21 $\text{mmol}^{1/2}\ \text{L}^{-1/2}$ on irrigated sites and from 0.25 to 1.13 $\text{mmol}^{1/2}\ \text{L}^{-1/2}$ on baseline sites in 2005. Average ESP values range from 4% to 8% on irrigated fields and 0.05–0.32% on baseline fields in 2005. Average EC values range from 4 to 7 dS m^{-1} on irrigated fields and 0.6–2.8 dS m^{-1} on baseline fields. Surface samples (to 30 cm) at the North irrigated site have significantly less cation exchange capacity (CEC) than the baseline site. Average values range from 13 to 16 $\text{cmol}_{(c)}\ \text{kg}^{-1}$ on the irrigated field to 27–28 $\text{cmol}_{(c)}\ \text{kg}^{-1}$ on the baseline field in 2005. Smectitic clay has cation exchange capacities of 8–15 $\text{cmol}_{(c)}\ \text{kg}^{-1}$ clay. Illite clays have much lower cation exchange capacities of 1–4 $\text{cmol}_{(c)}\ \text{kg}^{-1}$ clay (Drever, 1997). In general, Powder River Basin soils are dominated by 2:1 clays (like smectite) but also contain organic matter that contributes to the soil exchange capacity. The lower CEC on the North irrigated site may be related to a loss of organic matter. Measured pH values were the same between irrigated and baseline samples, as measured in saturated paste extractions, except for a slightly higher pH in irrigated as opposed to baseline surface (0–5 cm) samples (8.22 versus 7.84).

Trends seen at 30 cm depth in 2005 samples indicated that more information would be gained from deeper sampling, so another sample set was collected the following year. The 2006 measurements are single measurements and therefore reproducibilities cannot be determined. These samples serve instead as simply an indicator of trends at depths greater than those sampled in 2005. The 2006 sampling indicates that changes seen in shallow samples, such as higher SAR, ESP and EC on irrigated fields, are not seen at depths below 60 to 90 cm.

Calculations of the isotope ratio of the exchangeable Sr (Eqs. (3) and (4)) and the measured ratios of the extractable and soluble Sr are summarized in Table 3. Due to the much greater concentration of Sr in the extractable fraction as opposed to the soluble fraction, the isotope ratio of the exchangeable Sr is very similar to the extractable Sr isotope ratio. The fraction of extractable Sr that is

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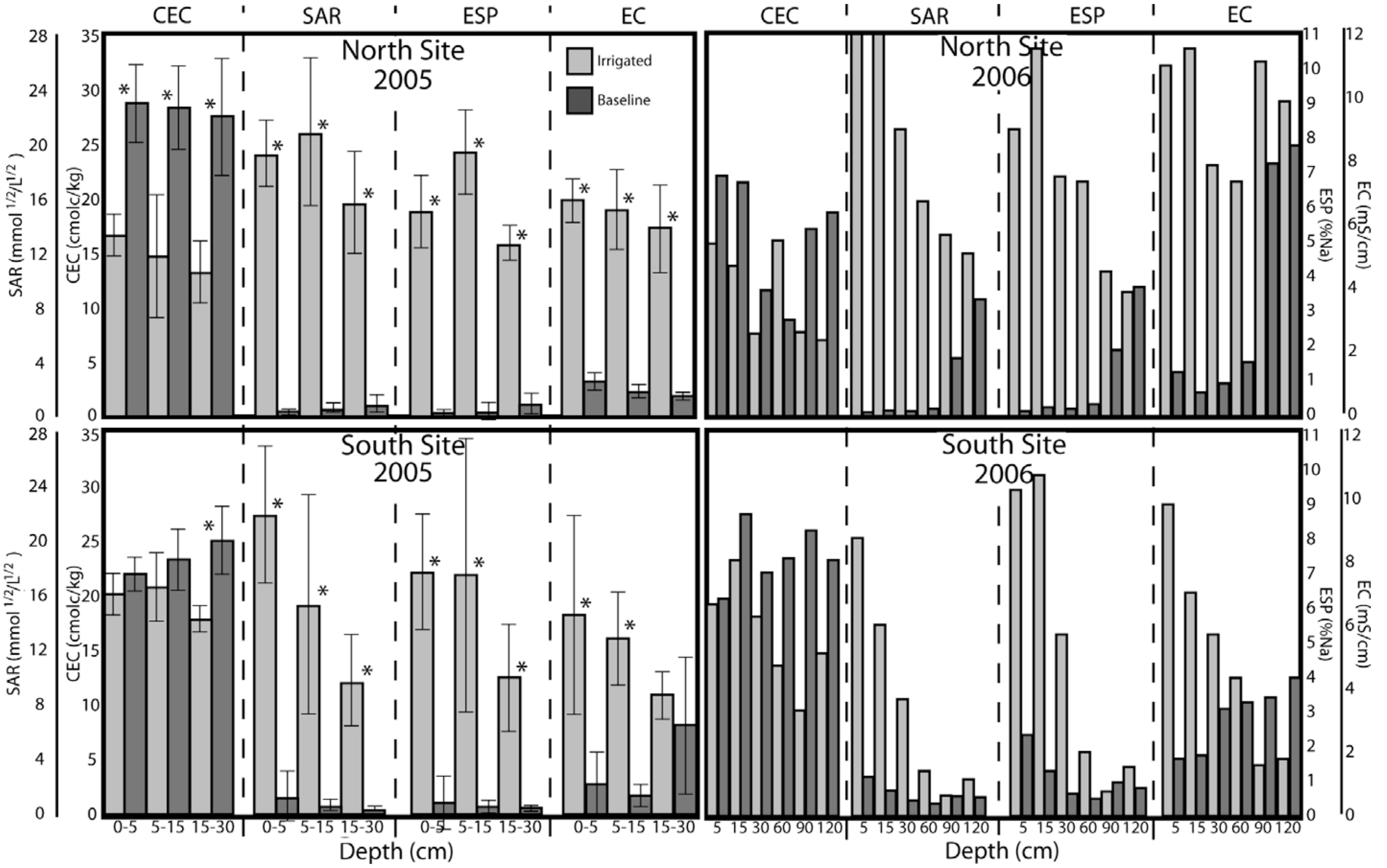

Fig. 2. August 2005 soil samples collected at depths of 0–5, 5–15 and 15–30 cm, $N = 5$. August 2006 soil samples collected at depths of 0–5, 5–15, 15–30, 30–60, 60–90 and 90–120 cm, $N = 1$. Units for cation exchange capacity (CEC) are $\text{cmol}_{(c)}\ \text{kg}^{-1}$ (near right axis), units for sodium adsorption ratio (SAR) are $\text{mmol}^{1/2}\ \text{L}^{-1/2}$ (far right axis), units for exchangeable sodium percentage (ESP) is percent sodium on soil exchange sites (unitless; near left axis), units for electrical conductivity (EC) are mS cm^{-1} (far left axis). * indicates statistically different ($p = 0.05$) by two-group *t*-test.

on the exchange sites ranges from 0.87 to 0.99 (last columns in Table 3) indicating that 1% to 13% of Sr is in soluble salt form.

The average and standard deviation in 2005 samples, and measured values of 2006 samples, of $^{87}\text{Sr}/^{86}\text{Sr}$ of exchangeable soil Sr are plotted on Fig. 3 by depth. Shaded areas represent the range in measured Sr isotope ratios for the gypsum amendment and the exchangeable Sr in baseline soil. In 2005 soil samples, the North and South irrigated site samples have significantly lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ($p = 0.05$) than the corresponding baseline samples throughout the sampled depth (30 cm). However, South irrigated site Sr isotope ratios increase with depth. In 2006 samples, the North irrigated site samples have lower Sr isotope ratios than baseline ratios throughout the sampled depth (120 cm); however, North Site baseline sample Sr isotope ratios decrease with depth, lessening the difference between the irrigated and baseline ratios. Strontium isotope ratios in surface samples in the 2006 South Site irrigated field are lower than the baseline fields; however, at depths >30 cm the irrigated soil is indistinguishable from baseline soil.

Table 4 presents the results from solving Eq. (5) for the fraction of Sr on the exchange sites that originated from gypsum. In 2005 samples, approximately half the Sr on the cation exchange sites is from the addition of gypsum to 30 cm at the North irrigated site and at the surface of the South irrigated site. Deeper samples at the South irrigated site show less influence of gypsum with only 20% and 10% of the Sr coming from gypsum. In 2006 samples, approximately half the Sr on the exchange sites comes from gypsum at the surface of the North irrigated site. Progressively less Sr on the exchange sites comes from gypsum in deeper samples with 10–20% originating from gypsum in soil deeper than 30 cm. South irrigated site samples from 2006 are similar to South Site 2005 samples in that only the surface sample has a significant contribution of Sr from gypsum. For Sr in the South irrigated site surface sample in 2006 approximately 30% is from gypsum; less than the 50% Sr from gypsum measured in the 2005 surface sample. This may be due to using a perhaps anomalously low baseline ratio (0.71009) in the calculation for "*f*". If the irrigated Sr isotope ratio for the 2006 South irrigated site surface sample is compared to the average ratio measured in 2005 surface sample (0.71254), the fraction of Sr contributed by gypsum is approximately 68%. Another potential cause for the lower fraction of Sr is that no gypsum was applied to the South irrigated site in 2006. Deeper samples show almost no Sr from gypsum; negative values of "*f*" in Table 4 result from natural variation in the Sr isotope ratio.

4.3. Vegetation

Strontium isotope ratios of grasses collected on irrigated fields show overall lower ratios compared to grasses collected on baseline fields (Fig. 4). These lower values reflect the influence of the gypsum amendment which contributes a much lower (0.7074) Sr isotope ratio than does the local soil's exchangeable Sr pool (0.712–0.713). Not all baseline vegetation samples fall within the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured for the baseline soil. Samples with higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the baseline soil, such as some found on the South baseline field, may be due to deeper roots accessing exchangeable Sr not measured in the near-surface sampling. Carter et al. (2007) measured the Sr isotope ratios for the

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Table 3
Strontium isotope ratios and concentrations for extractable, soluble, and exchangeable cations in soils from North and South Sites.

Field Site	Sampling interval	Extractable				Soluble				Exchangeable				*f*	
		$^{87}Sr/^{86}Sr$		Sr (cmolc/kg)		$^{87}Sr/^{86}Sr$		Sr (cmolc/kg)		$^{87}Sr/^{86}Sr$		Sr (cmolc/kg)			
		2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	2005	2006
North site															
Irrigated	0–5	0.70946 (5)	0.70916	0.0145 (26)	0.0887	0.70955 (6)	0.70927	0.0014(1)	0.0036	0.70945 (5)	0.69782	0.0131(25)	0.0851	0.90	0.96
	5–15	0.70997(2)	0.7101	0.0091 (9)	0.0487	0.71010(2)	0.71028	0.0011(2)	0.0035	0.70994 (2)	0.69192	0.0079 (7)	0.0453	0.88	0.93
	15–30	0.71000(4)	0.71029	0.0123(33)	0.0381	0.71017(4)	0.71044	0.0016(7)	0.002	0.70998 (4)	0.69417	0.0107(27)	0.0361	0.87	0.95
	30–60		0.71034		0.0686		0.71044		0.0041		0.69971		0.0645		0.94
	60–90		0.71043		0.0497		0.71058		0.005		0.69349		0.0448		0.9
	90–120		0.7104		0.053		0.71064		0.005		0.68479		0.0481		0.91
Baseline	0–5	0.71208(5)	0.7114	0.0082 (4)	0.0357	0.71212(5)	0.71146	0.0005(1)	0.0009	0.71208(5)	0.70469	0.0078 (5)	0.0348	0.94	0.97
	5–15	0.71227(4)	0.71183	0.0093 (17)	0.0469	0.71239(4)	0.7121	0.0003(1)	0.0005	0.71227 (4)	0.68437	0.0090(16)	0.0463	0.96	0.99
	15–30	0.71224(5)	0.71134	0.0107(20)	0.0421	0.71231(5)	0.71199	0.0003(1)	0.0007	0.71224 (5)	0.64619	0.0104(19)	0.0415	0.98	0.98
	30–60		0.71089		0.0374		0.71149		0.0012		0.64901		0.0362		0.97
	60–90		0.71071		0.0722		0.7108		0.0071		0.70016		0.0651		0.9
	90–120		0.711		0.0687		0.71115		0.0054		0.69528		0.0634		0.92
South site															
Irrigated	0–5	0.71002(8)	0.70931	0.0158(44)	0.0957	0.71027(9)	0.7092	0.0020 (7)	0.0046	0.70998 (8)	0.71994	0.0138(38)	0.0912	0.88	0.95
	5–15	0.71178(5)	0.71137	0.0096 (27)	0.0406	0.71202(5)	0.71164	0.0010(5)	0.0021	0.71175(5)	0.68365	0.0085 (22)	0.0385	0.89	0.95
	15–30	0.7123 (4)	0.71224	0.0083 (12)	0.0404	0.71235(4)	0.71253	0.0007(2)	0.0019	0.7123 (4)	0.68294	0.0076(11)	0.0385	0.91	0.95
	30–60		0.71181		0.0584		0.71244		0.0026		0.6462		0.0559		0.96
	60–90		0.71261		0.0401		0.71281		0.001		0.69256		0.0391		0.98
	90–120		0.71264		0.0615		0.7128		0.0013		0.69723		0.0602		0.98
Baseline	0–5	0.71256(5)	0.71009	0.0091 (11)	0.0581	0.71274 (4)	0.71025	0.0004 (5)	0.0011	0.71254(5)	0.69424	0.0086 (6)	0.057	0.95	0.98
	5–15	0.71277(1)	0.71207	0.0088(6)	0.0464	0.71292(1)	0.71216	0.0002 (2)	0.001	0.71276(1)	0.70387	0.0086 (6)	0.0454	0.98	0.98
	15–30	0.71285(1)	0.71188	0.0097(12)	0.0519	0.71302(1)	0.71211	0.0009(3)	0.0024	0.71283(1)	0.68836	0.0088 (9)	0.0495	0.91	0.95
	30–60		0.71279		0.063		0.71296		0.0033		0.69517		0.0598		0.95
	60–90		0.71275		0.0645		0.71292		0.0035		0.69478		0.0611		0.95
	90–120		0.7127		0.0682		0.7129		0.0048		0.69082		0.0634		0.93

2005 values are the average of five replicates. Parenthetical values are the standard deviation ($\times 10^{-4}$) of 2005 samples, $n = 5$.

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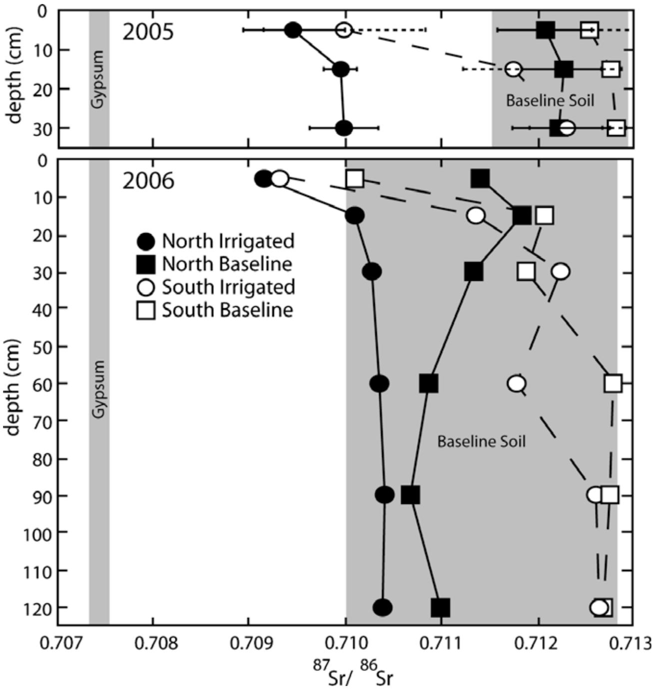

Fig. 3. Strontium isotope ratios of exchangeable Sr with depth. North irrigated and baseline site samples are solid circles and squares, respectively. South irrigated and baseline site samples are open circles and squares, respectively. Grey shaded areas represent the range of Sr isotope ratios measured for the gypsum amendment and the exchangeable Sr in baseline soil. Shaded areas for baseline soil represent the range of isotope ratios measured for the respective years. August 2005 samples, $N = 5$, all irrigated/baseline pairs are statistically different ($p = 0.05$) by two-group *t*-test; August 2006 samples, $N = 1$.

Table 4
Average $^{87}Sr/^{86}Sr$ ratios for irrigated and baseline samples and fraction of Sr contributed by gypsum.

Sampling year	Depth interval (cm)	North			South		
		Irrigated	Baseline	*f*	Irrigated	Baseline	*f*
Exchangeable strontium							
2005	0–5	0.70945	0.71208	0.56	0.70998	0.71254	0.50
	5–15	0.70994	0.71227	0.48	0.71175	0.71276	0.19
	15–30	0.70998	0.71224	0.47	0.71230	0.71283	0.10
2006	0–5	0.70915	0.71140	0.56	0.70931	0.71009	0.29
	5–15	0.71009	0.71182	0.39	0.71136	0.71207	0.15
	15–30	0.71028	0.71133	0.27	0.71223	0.71187	−0.08
	30–60	0.71033	0.71087	0.15	0.71178	0.71278	0.19
	60–90	0.71041	0.71069	0.09	0.71260	0.71274	0.03
	90–120	0.71038	0.71099	0.17	0.71264	0.71268	0.01

2005: Sr isotope ratios are average values for exchangeable Sr in five replicates. 2006: Sr isotope ratios of exchangeable Sr measured in one sample. The "*f*" term represents the fraction of strontium contributed by gypsum to the exchange complex assuming a strontium isotope value of 0.7074 for gypsum.

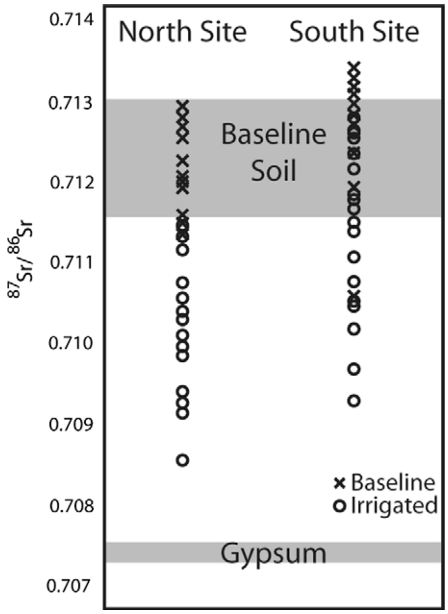

Fig. 4. Strontium isotope ratios for irrigated and baseline vegetation. Grey shaded areas represent the range of Sr isotope ratios for exchangeable Sr in baseline soil and dissolved gypsum.

Powder River bed load and water as 0.7143 and 0.7128, respectively. Additionally, the Sr isotope ratios for Beaver Creek bed load and water were 0.7160 and 0.7134, respectively (Carter et al., 2007). If native vegetation accesses these water sources one would expect that the North Site vegetation (near the Powder River) would have lower Sr isotope ratios than the South Site (near Beaver Creek) as depicted in Fig. 3. Beaver Creek's Sr isotope ratio of 0.7134 may explain why the vegetation at the South Site has a higher $^{87}Sr/^{86}Sr$ ratio than the measured Sr isotope ratios in the soil. Unusually low $^{87}Sr/^{86}Sr$ ratios found in baseline vegetation samples, such as one on the South baseline field, may be due to the persistently high winds in this area spreading the gypsum amendment further than intended. A description of major ion and trace element concentrations of irrigated and baseline vegetation can be found in Brinck (2007).

5. Discussion

5.1. Adsorption of calcium and vegetation uptake

Strontium, a proxy for Ca, introduced from gypsum applied to soils irrigated with CBNG produced water is retained on the soil cation exchange complex to varying degrees. The degree to which the Ca is adsorbed on the cation exchange sites depends upon a number of factors including how much gypsum and irrigation water have been applied. The North Site, by summer of 2006, had undergone irrigation for 4 a and has therefore had more irrigation water and gypsum applied than the South Site, which has undergone irrigation for just one full year. Strontium from gypsum is observed on the exchange sites of the soil to a depth of 30 cm on the North irrigated field, whereas the incorporation of Sr from gypsum is only seen in the surface soils (0–5 cm) of the South irrigated field (Fig. 3). A smaller fraction of the Sr on the exchange sites originated from gypsum in 2006 than in 2005 at both the North and South sites (Table 4). This is most likely because less gypsum was added to the soil in 2006 than in 2005 and less water put on the field for irrigation. This may indicate that Ca cycles in this system fairly quickly; a measurable amount of the available Ca from gypsum being taken up by the vegetation and replaced by local Ca in just one season.

Deeper sampling revealed that the Sr isotope ratio of North Site baseline soil exhibits some variability with depth. Samples collected below 30 cm have a lower Sr isotope ratio (0.711) than the shallower samples (0.712). It is possible that deep-rooted plants may be accessing the Sr on the exchange sites from deep in the soil profile and hydraulically lifting this Sr to be incorporated onto exchange sites near the surface (Chapin et al., 2002). Potentially, then, not all the low isotope ratio Sr came from gypsum but was perhaps brought up from deeper sources. If this is happening, then

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the calculated fraction of Sr from gypsum in surface samples (to 30 cm) at the North Site (0.27–0.56) is a maximum. In contrast, the South Site baseline soil profile has fairly consistent Sr isotope ratios throughout (0.7125–0.7128) except in shallow samples from the 2006 sampling. There may be more heterogeneity in surface soil at the South Site than at the North Site, or the low Sr isotope ratios from the surface samples at the South Site baseline field may be due to the consistently high winds carrying the gypsum amendment beyond its intended application area.

The Sr isotope ratio of vegetation collected on irrigated fields was lower overall than that of vegetation collected on baseline fields. Vegetation on the irrigated fields, therefore, is taking up Sr, and by extension Ca, that originated from the gypsum amendment (Fig. 4). This is further evidence that the gypsum is supplying Sr to the soil's exchange complex and it is being held in a plant-available form.

5.2. Chemical parameters

The gypsum amendment is intended to maintain a soil chemical balance. While the SAR, ESP and EC values are higher on irrigated soil than on baseline soil (Fig. 2), more work is required to determine if these values are endangering plant and soil health. SAR, as a soil water measurement, can only predict the potential for dispersion of soil structure when analyzed in conjunction with soil water EC values. Threshold values of EC and SAR at which soil will remain flocculated is soil specific. Several studies have been conducted on various types of soils to determine these threshold values (Barzegar et al., 1994; Rengasamy et al., 1984; Ward and Carter, 2004). To make accurate predictions of the threshold values at which Powder River Basin soil will remain flocculated, a soil specific study would need to be done; however, Rengasamy et al. (1984) found that for a composite soil sample of a variety of soil types, soil would remain flocculated with SAR values of around 20 when EC values were above around 2.5 dS m^{-1}. Although the SAR values in North and South irrigated fields are elevated above baseline, there are also correspondingly elevated EC values such that soil structure may be protected in these fields (Fig. 2). ESP on both North and South irrigated sites is below 11%. As a general rule, Na begins to affect the soil structure when ESP approaches 15%, however these measurements were made on composite soil samples of higher EC and sodification effects can be found at much lower ESP values depending upon the soil type (Qadir and Schubert, 2002; Sumner et al., 1998; US Salinity Laboratory Staff, 1954). Work that was done by King (2006) at the North Site showed a reduction in infiltration rate on the North irrigated field from 2003 to 2004. However, King (2006) measured higher ESP values in 2004 (20–30%; significantly higher than baseline to 120 cm) than measured in this study, which perhaps prompted more intensive management leading to the lower ESP values measured in this study in the following 2 years. Further measurements of soil physical parameters should be made to see if infiltration has improved with the lower ESP values measured in this study. The EC on North and South Site irrigated soils, ranging from 1.33 to 11.5 dS m^{-1}, is near the tolerance limit for salt tolerant plants. Barley (*Hordeum vulgare*), which is planted on the North and South Sites, is tolerant to EC values of 8.0 dS m^{-1}. Alfalfa (*Medicago sativa*), which is planted on the North Site, is less tolerant with yields beginning to decline at 2.0 dS m^{-1} (Essington, 2004).

Deep soil sampling in 2006 found SAR, ESP and EC parameters to be indistinguishable from baseline samples at depths below 90 cm on the North Site and 60 cm on the South Site (Fig. 2). These data agree with King's (2006) findings in 2004 at the North Site for SAR and EC. King (2006) found that soil chemistry was not statistically different at depths below 60 cm for SAR and 30 cm for EC. Samples collected near the beginning of managed irrigation with CBNG produced water show an initial increase in SAR, ESP and EC values as seen in 2005 South Site samples (after 6 months of irrigation) and 2004 North Site samples (after a year of irrigation; King, 2006). Later sampling, such as the 2006 samples at North and South Sites, are very similar to the samples collected earlier, indicating that after initial increases the salinity and sodicity levels stabilized.

Lower CEC levels on the North Irrigated Site (Fig. 2) may be due to mobilization or dissolution of organic matter. Black water was observed on the North Site in areas of ponding, which is an indication of mobilized organic matter. Martinez et al. (2002) speculate that smectitic clays are likely to lose surface organic matter to leaching in Na/Ca solutions because smectite attracts Ca more strongly than does the organic matter, leaving the organic matter to interact with the Na. In column studies, 27.4% of the original organic matter was lost due to leaching in smectite dominated clays interacting with Na/Ca solutions (Martinez et al., 2002).

6. Conclusions

Strontium isotopes have been used in ecosystem studies for many years; this study shows that they also effectively evaluate techniques used to ameliorate sodic soils. The movement and incorporation onto the exchange complex of Sr from the gypsum amended to CBNG irrigated soils was traced using Sr isotopes. This Sr tracing technique could be used in other situations where soils are at risk of sodification, or the local soil–plant Ca cycle may be disrupted.

Gypsum amended to soil irrigated with CBNG co-produced water is effective in supplying a source of Sr and Ca to the exchange sites of the soil. The effect of adding S to the surface was inconclusive in that during the study period it did not lower the pH of the soil water. Perhaps a more effective way to lower the pH of the irrigation water and convert HCO_3^- to CO_2 is acidifying the water itself prior to use in irrigation systems through use of S-burners, which is currently being done in several irrigation projects in the Powder River Basin (King, 2006).

Despite having a source of Ca that is incorporated onto the exchange sites of the soil, the amount of Na occupying exchange sites increased following irrigation with CBNG co-produced water. This is reflected in the SAR value of the irrigated field's soil water, which was elevated over baseline. It is possible that in the event of a heavy rain event or the cessation of irrigation, the EC may drop below the threshold needed to maintain flocculation. To avoid degradation in soil structure, care should be taken to keep SAR levels low enough that natural salt levels will maintain a compressed double layer. Baseline EC values measured in the baseline sites indicate that natural salt levels are around 1–2 dS m^{-1}. At these EC levels, soil may have SAR values around 10–15 with low risk of dispersion (Rengasamy et al., 1984); however a soil specific study must first be done to ensure the correct threshold SAR values have been identified. To achieve these lower soil SAR levels, it may be necessary to lower the initial Na levels of the irrigation water prior to application. Several systems which will remove Na from water are being tested (Vance et al., 2007).

Acknowledgements

Funding for this project came through the DOE grant ‘‘Research and Development Concerning Coal Bed Natural Gas: CBNG Produced Waters Investigations’’, Award DE-FC26-06NT15568 – Task 4, to Carol Frost. Additional funding came from an EPA STAR Fellowship to Elizabeth Brinck. The authors would like to thank Anadarko Petroleum and BKS Environmental for their cooperation during this study. We would also like to thank Dr. Nilantha

Hulugalle and an anonymous reviewer for their help improving the quality of this paper, and Dr. Steve Boese, Dr. Jeffrey Cline, Dr. Girisha Ganjegunte, Mr. Chris Jesse, Dr. Elise Pendall, and Dr. George Vance for their editorial reviews and laboratory help.

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Please cite this article in press as: Brinck, E., Frost, C. Evaluation of amendments used to prevent sodification of irrigated fields. Appl. Geochem. (2009), doi:10.1016/j.apgeochem.2009.09.001