

# USING STRONTIUM ISOTOPES TO EVALUATE CBNG IRRIGATION AMENDMENTS<sup>1</sup>

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**Abstract.** Water produced as a byproduct of coal bed natural gas (CBNG) production may be used for irrigation when its water quality permits. Produced water, which is typically sodium-bicarbonate type, may cause clay dispersion, potentially resulting in reduced soil permeability. These effects may be mitigated by the application of sulfur and gypsum amendments to the soil surface. Both contribute calcium to the soil's cation exchange complex; gypsum through dissolution and sulfur by bringing naturally occurring calcite into solution.

In this study, soil samples were collected from two irrigated and two non-irrigated fields along the Powder River in northeast Wyoming. At the time of sampling, one field had been irrigated for three years, while the other had undergone irrigation for three months. We used the isotopic ratio of naturally-occurring strontium of the soil, irrigation water and amendments to trace the influence of gypsum amendments on the soil column. We show that because of strontium's chemical similarity to calcium, the strontium isotopic ratio identifies inputs, changes to the calcium cycle, and downward movement of calcium from gypsum in fields irrigated with CBNG-produced water. Gypsum supplies more of the calcium on the cation exchange complex in fields that have undergone irrigation and gypsum application for three years compared to those with irrigation and amendment application for three months. Calcium supplied by gypsum is apparently downwardly mobile in soil to depths of up to 30 cm on the field irrigated for three years. Prolonged application of gypsum may help the clays maintain a plant available source of calcium which will help mitigate some of the negative effects of using sodium rich CBNG water for irrigation. The conclusions drawn by this study may help design future treatment options for CBNG produced water beneficial uses, while still protecting the integrity of the soil to which it is applied.

Additional Key Words: calcium cycle and isotopic tracers

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## **Introduction**

Coal bed natural gas (CBNG) production in the Powder River Basin is an increasingly important influence on Wyoming's economy and environment. Powder River Basin CBNG development includes depressurizing a coal seam through dewatering and collecting the natural gas, almost entirely composed of methane, in an annular pipe (DeBruin et al., 2004). The produced water may be discharged to existing drainages, surface impoundments and occasionally to irrigation systems (King, 2006). Wyoming law requires beneficial use of produced water (Wyoming statute 41-3-101) and in this semi-arid area this includes viable agricultural uses such as growing hay for livestock (WLSO, 2006). Irrigation could potentially allow land owners to increase the number of ranch animals per acre by increasing the available fodder.

One measure of the quality of irrigation water is the sodium adsorption ratio (SAR) which is the ratio of Na to Mg and Ca (Essington, 2004). In general, CBNG water has high SAR values ranging from a median of 8.8 to a maximum of 68.7, which would generally preclude its use as a source of irrigation water (Rice et al., 2002). In high concentrations, Na in the applied water will displace Ca from exchange sites on soil clays. The larger hydrated radius of Na can cause the soil organic matter and clay to disperse, reducing soil structure and therefore infiltration capacity (Essington, 2004). Additionally, Na is not a plant nutrient and through displacing Ca can cause Ca deficiencies in plants. To counteract the negative effects of using high SAR water for irrigation, gypsum ( $\text{CaSO}_4$ ) may be applied to the surface of fields irrigated with CBNG water. Gypsum dissolution adds Ca and  $\text{SO}_4^{-2}$  ions to the soil. If these  $\text{Ca}^{+2}$  ions are incorporated onto the cation exchange complex (CEC) of the soil, they have the potential to prevent sodification of the soil. In many CBNG irrigation situations, elemental sulfur (S) is also applied to the surface to lower the pH of the soil thereby bringing local calcite ( $\text{CaCO}_3$ ) into solution. Dissolution of calcite provides a Ca source that will also help protect the soil from sodification. However, monitoring the effects of S amendments is outside the scope of this study.

Strontium (Sr) isotopes have been shown to be effective tracers of the Ca cycle (Capo et al., 1998; Blum et al., 2000). The natural variation of Sr isotopes in geologic material is due to the decay of the unstable 87-rubidium isotope which results in an  $^{87}\text{Sr}/^{86}\text{Sr}$  value that fingerprints distinct geologic material. The strontium isotopes  $^{87}\text{Sr}$  and  $^{86}\text{Sr}$  are not fractionated in biogeochemical processes such as evaporation or plant uptake (Blum et al., 2000). Most importantly, strontium's chemical similarity to calcium allows Sr to replace Ca in natural processes and can therefore be used as a natural isotopic tracer of the Ca cycle. We have used the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the gypsum to follow fate of the introduced Ca from the gypsum amended to CBNG irrigated fields.

## **Field Sites**

Two fields currently being irrigated with CBNG produced water were chosen for this study (Fig. 1). The North Site is a 40 acre center pivot lying near the Powder River about five kilometers south of Interstate-90. It has undergone intermittent irrigation since the summer of 2002 and has been planted with alfalfa and barley. The South Site is a 20 acre center pivot lying

near the confluence of Beaver Creek and the Powder River about eleven kilometers south of Interstate-90. It has undergone intermittent irrigation since June of 2005 and is planted with barley.

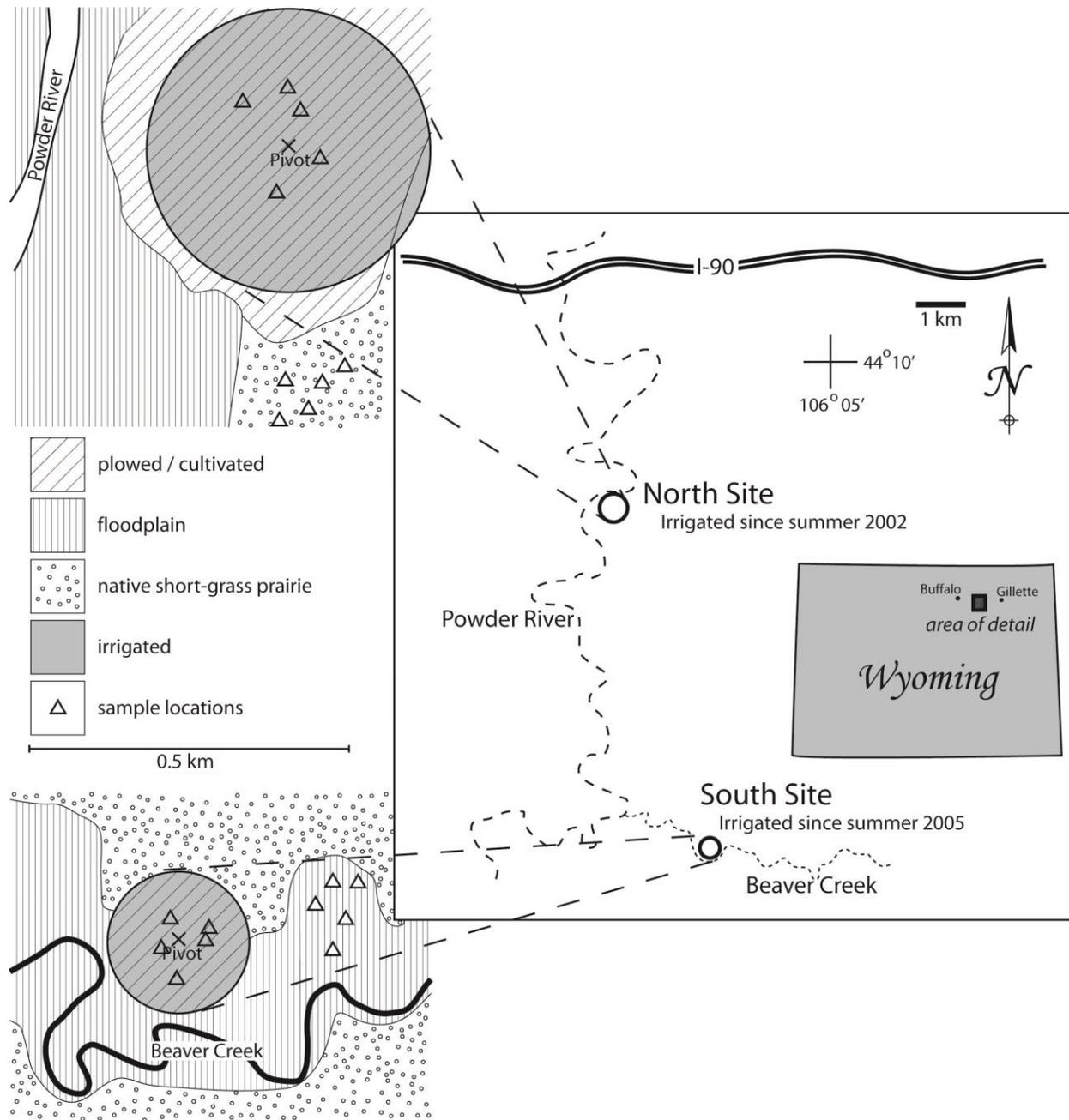


Figure 1. Approximate location of irrigated field sites (in grey) and sample locations (triangles). Areas chosen for baseline studies are shown by sample locations outside the irrigated field.

In general, these irrigated fields are amended with 2.2 to 4.5 Mg/ha/year (1 to 2 tons/acre/year) of sulfur and 11.2 to 15.7 Mg/ha/year (5 to 7 tons/acre/year) of gypsum. In 2005, North Site received 11.2 Mg/ha (5 tons/acre) gypsum in March, 2.8 Mg/ha (1.25 tons/acre) gypsum in July, and 1.2 Mg/ha (0.55 tons/acre) of S in July. The 2005 irrigation season began in

May at North Site. North Site received 25.4 cm (10.02 inches) of water for the season; however 17.7 cm (6.99 inches) of this came after the soil sampling in August. In 2005, South Site received 4.5 Mg/ha (2 tons/acre) of gypsum in March and 5.6 Mg/ha (2.5 tons/acre) in July. Sulfur was applied at South Site in July at a rate of 2.5 Mg/ha (1.1 tons/acre). Irrigation began in June at South Site with a total 33.1 cm (13.05 inches) of irrigation water added during the season with 15.1 cm (5.95 inches) of water added after the soil sampling in August.

As a control, natural grass lands adjacent to each irrigated field were chosen for study hereafter referred to as North Site Baseline and South Site Baseline. The location of these fields is indicated by triangles outside the irrigated field on Fig. 1. 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. 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.

## Methods

Soil samples were collected on each of the four fields (two irrigated, two non-irrigated) in August, 2005. Sample locations are shown by triangles in Fig. 1. On each site, five random locations were chosen and sampled by depth using a hand auger. Samples were collected from 0 to 5 cm, 5 to 15 cm, and 15 to 30 cm. Individual depth samples were homogenized and stored in one-pint air-tight plastic bags.

Upon returning to the geochemistry laboratory at the University of Wyoming, the water content of the soil was determined by weighing out the moist soil, drying the sample for 48 hours at 40.5 °C (105 °F) and reweighing the dry sample. The entire soil sample set was then dried indoors for two weeks and sieved through 2 mm screens.

Ammonium acetate (NH<sub>4</sub>OAc) extractions were performed in the Soil Chemistry Laboratory at the University of Wyoming. Five grams ( $\pm 0.05$ g) each of the dried, sieved soil samples were measured into clean 50 ml centrifuge tubes. Thirty-three milliliters of 1N NH<sub>4</sub>OAc solution was added to each tube before being placed on the reciprocating shaker for 5 minutes. The tubes were then placed in a centrifuge for 10 minutes at 2000 rpm. The resulting supernatant was filtered into a 100 ml volumetric flask. The addition of NH<sub>4</sub>OAc through filtering the supernatant was repeated twice more (Sumner and Miller, 1996).

The extracted cations in the NH<sub>4</sub>OAc were isolated through cation exchange columns filled with strontium specific resin. The resulting Sr samples were analyzed for <sup>87</sup>Sr/<sup>86</sup>Sr on a solid source thermal ionization mass spectrometer at the University of Wyoming. The internal precision of <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratio measurements is  $\pm 0.00001$ . 76 analyses of NBS 987 Sr standard measured during the course of this study gave an average value of <sup>87</sup>Sr/<sup>86</sup>Sr =  $0.71026 \pm 0.00002$  (2 standard deviations). All analyses were normalized to an <sup>86</sup>Sr/<sup>88</sup>Sr ratio value of 0.1194. Analytical blanks were less than 0.2 ng, negligible compared to sample sizes of at least 0.1 microgram Sr.

Two tenths gram of the gypsum amendment was dissolved in 5 mL 6N HCl and an additional 0.2 g gypsum was dissolved in 5 mL distilled water. These mixtures were allowed to sit on a heating element for 72 hours. One milliliter of each solution was dried in an evaporator. The Sr in the samples was separated using Sr specific resin and analyzed for  $^{87}\text{Sr}/^{86}\text{Sr}$  on a solid source thermal ionization mass spectrometer.

### Results

The five replicates of the  $^{87}\text{Sr}/^{86}\text{Sr}$  values for the three sampled depths on the four fields were averaged and plotted with their standard deviation (Fig. 2). The baseline samples are represented by squares: solid for North Site, open for South Site. For all depths, the North Site baseline field samples range from 0.7120 to 0.7125 while the South Site baseline samples are approximately 0.7130. This nearly vertical distribution of points indicates that the source of calcium is uniform throughout the sampled depths. The different  $^{87}\text{Sr}/^{86}\text{Sr}$  values (0.7125 for North Site and 0.7130 for South Site) are not unusual given the placement of the baseline fields. North Site is within the Powder River watershed, while South Site is in the Beaver Creek watershed. Each will have slightly different sources of sediment.

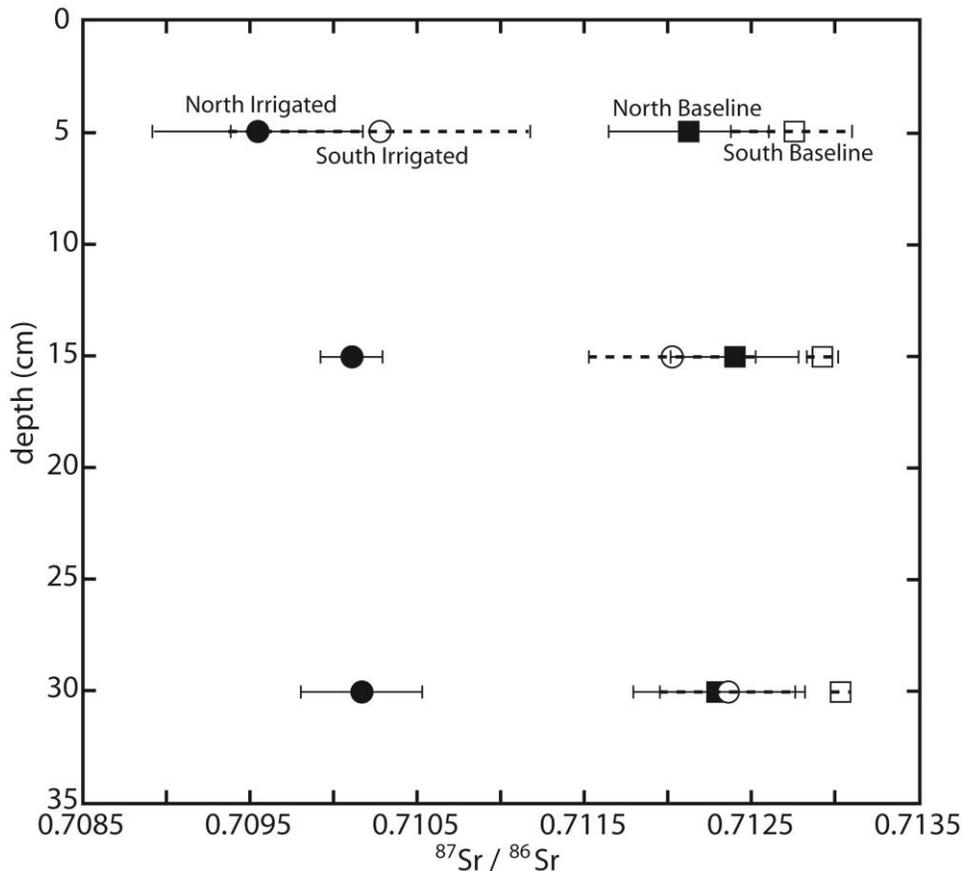


Figure 2.  $^{87}\text{Sr}/^{86}\text{Sr}$  of soil samples by depth. Solid circles and solid squares represent the North Site irrigated field and baseline respectively. Open circles and open squares represent the South Site irrigated field and baseline respectively. Error bars are one standard deviation.

There is a significant difference between the two irrigated fields in the amount of Sr from gypsum on the exchange sites, as shown in Fig. 2. The irrigated fields are represented by circles in Fig. 2: solid circles for North Site and open circles for South Site. The three sampled depths of the North Site irrigated field all fall within 0.7095 and 0.7105. The distribution of samples in the North Site sample set is not quite vertical, implying that the source of calcium is not entirely homogenous throughout the sampled depth. However, all samples are less radiogenic (lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio) than the associated North Site Baseline field (solid squares). The 0-5 cm sample is the least radiogenic of the three sampled depths.

Similarly, the shallowest sample (0-5 cm) on South Site irrigated sample set (open circles) is less radiogenic at 0.7105 than the two deeper samples of 0.7120 and 0.7125. The distribution of irrigated field South Site  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios is not vertical, but is less radiogenic at all depths than the associated baseline field (open squares) and more radiogenic than the irrigated North Site field.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the gypsum amendment is 0.70752 for both the samples dissolved in HCl and distilled water. This value is measurably different than the baseline values of 0.7125 and 0.7130. The mixing of two isotopic end-members, such as Sr from gypsum and local soil Sr, will result in an intermediate value such as those found on the irrigated field sites.

### **Discussion**

The samples taken from the irrigated sites (circles) have less radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios than those samples collected on the associated control sites (squares) at all depths; however the magnitude of shift varies by the length of time each field was irrigated with CBNG co-produced water. We interpret this shift in strontium isotope ratio to reflect the influence of the gypsum amendment because the irrigated soil samples show a less radiogenic Sr isotope ratio closer to that of the gypsum amendment value 0.70752. The gypsum is applied at the soil surface and is not tilled into the subsurface; for it to reach 30 cm depth it must have been brought into solution by irrigation water or rain and infiltrated to this depth. The extraction by  $\text{NH}_4\text{OAc}$  includes both soluble and exchangeable cations, so at any of the sampled depths the Sr which results from the dissolution of gypsum may either be incorporated on to the CEC or present as a soluble salt.

North Site, which had been irrigated for three years at the time of sampling, shows a larger shift in Sr isotope ratio from the control site for all three depths than does South Site which had only been irrigated for three months. The large shift seen at the surface at South Site (Fig. 2, Table 1) is most likely due to its direct contact with the gypsum amendment; additionally the extraction process would incorporate un-dissolved surface gypsum in the analysis. The samples taken at depth, however, do not show as great shift from the control Sr isotope values as does the surface sample. We interpret this to mean that very little of the Sr from the gypsum has infiltrated below 5 cm. In contrast, North Site which has undergone irrigation for three years shows much more influence from the gypsum at depth.

During the 2002 to 2004 irrigation seasons at North Site, the field received approximately 120 cm (50 inches) of irrigation water. In the 2005 irrigation season by the time of sampling, North Site had received an additional 7.7 cm (3.03 inches). In contrast South Site had only received 18 cm (7.1 inches) of irrigation water by the time of sampling. Approximately 130 cm of irrigation water at North Site allowed the Sr from the gypsum to infiltrate to at least 30 cm. South Site shows very little influence of gypsum below 5 cm after 18 cm of irrigation.

By using a two end member mixing model (eq. 1) we are able to estimate the relative contribution of gypsum as a source of Sr in the soil (Table 1):

$$\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_{\text{Irrigated}} = \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_{\text{Gypsum}} (f_{\text{Gypsum}}) + \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_{\text{Control}} (1 - f_{\text{Gypsum}}) \quad (1)$$

Table 1. Fraction of extractable Sr contributed from gypsum for average  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  values.

Sampling interval	Irrigated Field	
	North	South
0 to 5 cm	0.56	0.47
5 to 15 cm	0.47	0.17
15 to 30 cm	0.45	0.12

On the site irrigated since 2002, North Site, approximately one-half of the strontium originated from the gypsum amendment, whereas on South Site, the site irrigated since 2005, only the top-most soil has approximately one-half of its Sr from gypsum. In the deeper samples at South Site, over eight-tenths of the Sr is still from local sources.

### **Conclusions and Future Work**

The amount of gypsum amended and quantity of irrigation water applied to a field appear to determine the depth to which calcium from gypsum will infiltrate. For the gypsum amendment to be effective in protecting soil structure, however, the Ca that results from the dissolution of the gypsum must be incorporated onto the CEC. The method used here extracts both the cations incorporated onto CEC as well as those in soluble salt form. In order to differentiate the relative contribution of each cation form we must determine how much of the Sr measured is incorporated onto the CEC as opposed to as a soluble salt. For this reason, future work will include saturated paste analysis which will allow measurements of the soluble fraction of cations, which can then be used to calculate the amount of Sr incorporated onto the cation exchange sites. Additionally, deeper sampling will allow identification of the extent to which the strontium from the gypsum has infiltrated. Future sampling will include samples to 120 cm in an effort to identify the maximum infiltration of Sr from gypsum. The combination of these analyses should help to evaluate the potential effectiveness of gypsum amendments to protect the soil structure.

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