Low Salinity Hydrocarbon Water Disposal Through Deep Subsurface Drip Irrigation: Leaching of Native Selenium

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Abstract A subsurface drip irrigation system is being used in Wyoming's Powder River Basin that treats high sodium, low salinity, coal bed methane (CBM) produced water with sulfuric acid and injects it into cropped fields at a depth of 0.92 m. Dissolution of native gypsum releases calcium that combats soil degradation that would otherwise result from high sodium water. Native selenium is leached from soil by application of the CBM water and traces native salt mobilization to groundwater. Resulting selenium concentrations in groundwater at this alluvial site were generally low (0.5–23 μg/L) compared to Wyoming's agricultural use suitability standard (20 μg/L).

Keywords coal bed methane, coal bed natural gas, produced water, sodium adsorption ratio

Introduction

Coal bed methane (CBM) is rapidly expanding worldwide as a source of energy. Production is achieved by drilling into a flooded, subsurface coal bed, pumping out water, and collecting the natural gas liberated as a result of reduced pressure in the bed. Volumes of co-produced water are largest during early development. CBM generates greater volumes of water per volume of gas compared to other natural gas resources. In 2011, 7.8×10^7 m^3 of water were produced in the Wyoming portion of the Powder River Basin (PRB; Wyoming Oil and Gas Conservation Commission 2012). As a result, management and disposal of produced water is an important challenge for developing CBM resources.

Waters produced with CBM in the PRB generally have Na-HCO_3 compositions. The waters have low to moderate salinity in the form of total dissolved solids (TDS 200–4000 mg/L), but often have relatively high sodium adsorption ratios (SAR 5.6–69). The SAR of a water or soil extract can be calculated according to equation 1 with $mmol^{½}$ $L^{½}$ as the resulting units, although common convention in reporting data is to omit them.

$$SAR=\frac{[Na^+]}{\sqrt{([Ca^{2+}]+[Mg^{2+}])}} \quad (1)$$

Waters with low salinity and high SAR can damage soil by dispersing clay particles, which results in breakdown of soil structure, crusting, and decreased infiltration and permeability (fig. 1). Such problems can be particularly severe for soils containing high percentages of expansive clays; such soils are common in the PRB. Interactions of SAR, salinity, and soil properties make thresholds for soil damage difficult to define, but significant problems are generally expected to occur with SAR >15.

Disposal of CBM waters in the PRB is most commonly achieved by placing them in unlined impoundments to evaporate and infiltrate into the subsurface. One issue with such impoundments is that the infiltrating waters can mobilize native salts, including Se-bearing salts, and negatively impact groundwater quality (Healy *et al.* 2011). Selenium mobilization

Fig. 1 *Photograph on the left shows the physical effects of raw CBM produced water on soil. To the left of the felt tipped marker is unaffected soil and to the right is soil on which CBM produced water was spilled. Photograph on the right shows an aerial view of the Headgate SDI site. Bare patches in fields are herbicide carryover from landowner treatment of noxious weeds prior to SDI installation.*

can be a particular concern because when it reaches the surface environment in sufficient concentrations the resulting bioaccumulation negatively impacts wildlife health (Skorupa 1998).

A desire to derive beneficial use from CBM waters while simultaneously disposing of them spurred the development of the deep subsurface drip irrigation (SDI) method studied here (Zupancic *et al.* 2008). By this method, CBM water is allowed to oxidize, degas and settle out in a surge pond, then acidified with H_2SO_4, and applied year-round to agricultural land through drip-tubing buried 0.92 m deep. Oxidation results in the loss of redox sensitive elements (*e.g.* Fe and As) while degassing increases pH through CO_2 loss. Acidification with H_2SO_4 removes alkalinity and thus combats the precipitation of calcite in soil which would otherwise result from irrigating with a $NaHCO_3$ type water. Losses of Ca^{2+} to calcite precipitation can drive SAR values in soil solution higher, exacerbating problems with clay dispersion. Installation of the drip tubing at 0.92 m helps retard the rise of SDI solutes to the soil surface and prevents frost damage during year-round operation. However, such deep placement necessitates that the crop planted in the fields be a deep-rooted perennial like alfalfa or grass.

Several studies have examined different aspects of these SDI systems in the PRB (Bern *et al.* 2013a, Bern *et al.* 2013b, Bern *et al.* accepted, Engle *et al.* 2011, Engle *et al.* submitted). Here we assess mobilization of native selenium from soil beneath fields at a site irrigated by the SDI system described above.

Site description and SDI operation

The Headgate Draw SDI site (fig. 1) is located in Johnson County, Wyoming, and was constructed on a series of alluvial terraces at the confluence of Crazy Woman Creek and the Powder River (Engle *et al.* 2011). Installation of the SDI system was completed in October 2008 and fields were planted with alfalfa. High density polyethylene tubing for water application was buried at the 0.92-m depth and spaced 1.4 m apart, with pressure compensating emitters located every 0.92 m along the tubing. A total of 81 ha were covered by the SDI system. Produced water was pumped to a surge pond at the site from dozens of CBM wells. Acidification of CBM water was achieved by in-line addition of H_2SO_4, resulting in an injectate pH of ≈ 6.1. Injectate was applied year-round at an average rate of 0.026 m/month in 2008 and 2009, and increased to 0.100 and 0.084 m/month in 2010 and 2011, respectively. Natural precipitation and injectate application combined provided 0.34 m less water than potential evapotranspiration demand in 2009, but 0.56 and 0.45 m more than potential evapotranspiration demand in 2010 and 2011, respectively (Bern *et al.* accepted). Initial depths to groundwater below the fields were 3.2 to 3.8 m.

Soils at the site are generally silt loams and sandy loams, typical for the alluvial terrace setting (Bern *et al.* accepted). Clay mineralogy was dominated by illite and smectite, and both calcite and dolomite were ubiquitous in soil. Although soil contained little gypsum above 1 m depth, gypsum concentrations were often >2 % in deeper soil and ranged up to 6.9 %.

As with other SDI operations of this type, the SAR of surface soil increased little in response to injectate application, but SAR of soil near the depth of the drip tubing increased substantially (Bern *et al.* 2013b, Bern *et al.* accepted). Preventing the increase of SAR at the soil surface is a significant advantage of the described SDI method over surface irrigation methods using similar CBM waters and also allows disposal of greater volumes of water (Johnston *et al.* 2008). With continued injectate application, problems with SAR at and below the soil surface might be predicted (Bern *et al.* 2013b). However, CBM water production from any given set of wells declines with time and the SDI sites are designed to be operated only for several years. As of late 2012, the Headgate Draw SDI system was transitioning to use waters from an adjacent stream.

Methods

Data presented here were collected as part of a larger research and monitoring project (Engle *et al.* 2011). Ceramic tipped suction lysimeters were installed at depths of 0.5, 1.0 and 2 m at three sites (21, 23 and 24) within SDI fields in October 2008. Lysimeter samples were collected four times between May 2009 and March 2011, but not all lysimeters yielded enough water on all dates for all planned analyses. Fourteen groundwater monitoring wells inside and outside the boundaries of the SDI fields were sampled quarterly starting in May 2008. Injectate pumped to the fields was sampled on the same schedule. Sampling methodology, analytical protocols, and QA/QC results for water chemistry are described in Geboy *et al.* (2011). The saturation index for gypsum was calculated using the PHREEQC software. Depth to groundwater was continuously monitored at three wells installed within SDI fields using *in situ* pressure transducers.

Soil cores were collected at three sites (21, 22 and 23) within SDI fields. Cores were collected in October 2008, prior to SDI operation (pre-SDI), and again in October 2011 after three years of operation (post-SDI). Selenium in soil was measured by extraction at 1:1 water soil ratio on selected depth increments. Depth increments were selected to represent the zone with highest pre-SDI salt content based upon extract electrical conductivity. Extracts were filtered to <0.2 µm and selenium was analyzed by hydride generation at the U.S. Geological Survey in Denver.

Results

Injectate had high concentrations of Na compared to Ca and Mg, giving it an average SAR value of 24 (Table 1). Average specific conductance of injectate was 2,550 µS/cm. The combination of high SAR and low specific conductance indicates that the water would cause moderate to severe infiltration problems due to clay dispersion if used for surface irrigation (Ayers and Westcot 1985). The Se content of injectate averaged only 0.6 µg/L, indicating low concentrations in both CBM produced water and the H_2SO_4 used for acidification.

Soil water collected by lysimeter had lower SAR values compared to injectate, with one exception (fig. 2). Generally, soil water SAR varied between 0.5 and 10, indicating a substantial decrease in the risk of clay dispersion once injectate had equilibrated with subsur-

pH	Spec. Cond. (μS/cm)	TDS (mg/L)	Alkalinity† (mg/L)	SAR	Se μg/L
6.1±1.0	2550 ± 500	2200 ± 300	560 ± 470	24 ± 5	0.6 ± 0.2

Na (mg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)
560 ± 81	17 ± 3	15 ± 9	13 ± 2	32 ± 33	790 ± 480

†mg/L as $CaCO_3$

Table 1 *Averages and standard deviations of chemical parameters for injectate water.*

face soil. The gypsum saturation index of injectate varied from -2.7 to -1.5. Saturation indices for soil water were higher and generally varied from -0.9 to 0.3, with many values close to zero.

Groundwater concentrations of SO_4^{2-} varied over a narrow range in most of the 14 individual monitoring wells with no obvious trends (fig. 3). Exceptions were two wells within SDI fields where SO_4^{2-} increased toward the end of the monitoring period, and another located outside that had high values early on that decreased with time. In contrast, Se in groundwater showed distinct trends that were remarkably correlated between wells (fig. 3). Concentrations rose to a first peak in the middle of the 2009 growing season, and then dropped over the winter. Concentrations rose again sharply in early 2010, continued to increase moderately through the growing season, then dropped abruptly by early 2011.

Groundwater levels in monitoring wells within the SDI fields also showed trends with time (fig. 4). Injectate application rates in 2009 produced only moderate rises in groundwater. Substantial increases in injectate application rates in 2010 and 2011 caused groundwater levels to rise more rapidly. Peaks in groundwater levels occurred in early spring of 2010 and 2011, with an intervening decrease that corresponded to the summer growing season.

Concentrations of water-extractable selenium in pre-SDI soil varied from 11 to 557 μg/kg, generally increasing by site in the order 21, 23, 22 (fig. 5). Post-SDI soil showed a much narrower range of concentrations, from 18 to 107 μg/kg and much less differentiation between sites.

Discussion

A crucial geochemical process in the SDI fields is indicated by the combination of gypsum saturation indices closer to zero and lower SAR values in lysimeter water as compared to injectate. Dissolution of native gypsum releases Ca^{2+} and lowers the SAR of injectate as it equilibrates with soil (Bern *et al.* 2013b). By lowering the SAR, and simultaneously raising the salinity, native gypsum dissolution reduces the risk of clay dispersion and associated problems with soil permeability. Acidification of injectate extends the duration of gypsum influence by combating losses of Ca^{2+} to calcite precipitation, and keeps SAR lower if gypsum becomes depleted (Bern *et al.* 2013b).

Injectate application has been shown to increase salinity in two of the three monitoring wells located within SDI fields, despite the fact that the injectate had a lower salinity than the native groundwater (Bern *et al.* accepted). However, trends in SO_4^{2-} in the larger dataset from 14 wells across the site were generally dif-

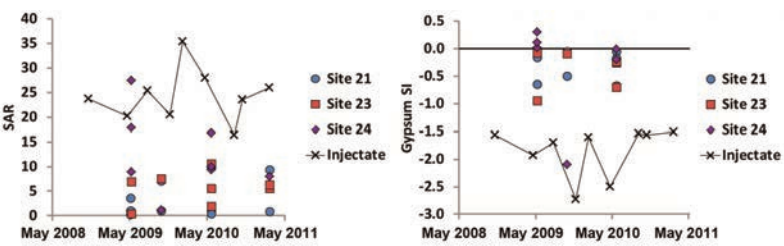

Fig. 2 *Time series of sodium adsorption ratio (SAR) and gypsum saturation index (SI) values for injectate and lysimeter samples.*

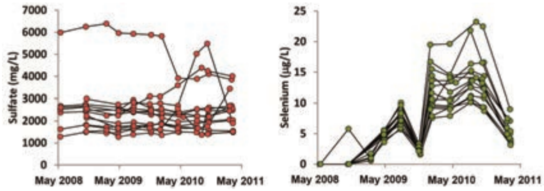

Fig. 3 *Time series of concentrations of sulfate and selenium in the 14 monitoring wells.*

ficult to discern (fig. 3). The same was true for the other major anions Cl^- and HCO_3^- (data not shown). Selenium, by contrast, showed dramatic shifts in concentration with conspicuous correlation in timing across all wells (fig. 3). A substantial decrease in soil concentrations of water-extractable Se between the pre-SDI and post-SDI cores (fig. 5) strongly suggests the SDI fields as the source of increased Se in groundwater.

Timing of the changes in groundwater Se concentrations relative to irrigation rates and groundwater levels can provide some insight into Se mobilization. Redox processes have the potential to confound such interpretations by conversions between soluble selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), and less soluble selenide (Se^{2-}). However, a lack of corresponding changes in SO_4^{2-} (fig. 3), with which SeO_4^{2-} shares redox similarities, allows Se concentration changes to be more confidently attributed to physical mobilization.

Initial increases in groundwater Se (fig. 3) corresponded to the moderate irrigation rates and rise of groundwater in 2009 (fig. 4). The Se peak in August of 2009 was likely generated by injectate leaching Se from soil directly beneath the drip tubing. Lower concentrations in the following winter may have reflected dispersion or dilution of the leached Se. The abrupt increase in groundwater Se in January 2010 correlated with an abrupt increase in injectate application rates. Subsequent moderate increases in Se occurred as groundwater levels first rose and saturated more soil, and then decreased due to crop water usage in the 2010 growing season. The sharp drop in groundwater Se over the 2010–2011 winter corresponded to another sharp rise in groundwater levels, again possibly reflecting dispersion or dilution. That decline, combined with decreased water extractable Se in soil (fig. 5), may indicate little potential for additional Se mobilization.

As was shown by a study of groundwater near a CBM impoundment (Healy *et al.* 2011), Se can trace native solute mobilization in the subsurface of the PRB. In contrast to the impoundment study, which found unusually high Se concentrations in groundwater (>300 µg/L), concentrations at Headgate Draw were rather moderate. Only three samples exceeded Wyoming's 20 µg/L of Se groundwater quality standard for agricultural use, the most sensitive of the state's groundwater selenium standards (Wyoming Department of Environmental Quality 2005). By comparison, all groundwater samples (pre- and post-SDI) exceeded the 200 mg/L agricultural suitability standard for SO_4^{2-} (fig. 3).

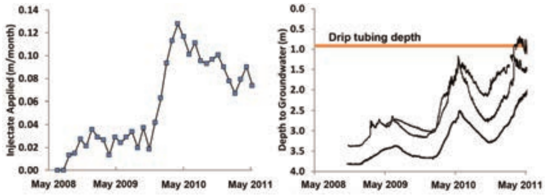

Fig. 4 *Time series of injectate application rates and, for three monitoring wells, depths to groundwater below SDI fields.*

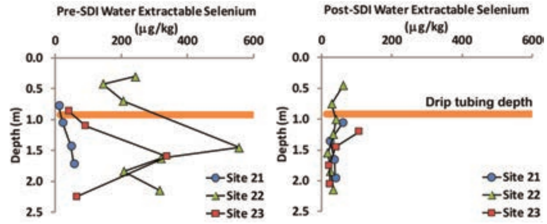

Fig. 5 *Depth profiles of water extractable selenium in SDI field soil before and after irrigation. Yellow line marks the depth of the drip tubing.*

Conclusions

High SAR values in injectate derived from CBM produced water were lowered by dissolution of native gypsum in subsurface soil. Lowering of the SAR values, and increasing electrical conductivity of soil waters, reduced the risk of soil permeability problems. Injectate application mobilized native selenium from the soils in the SDI fields and raised concentrations in groundwater. Selenium appears to be a good tracer for native salt mobilization in the PRB. Even at their peak, selenium concentrations at the Headgate Draw SDI site were generally below Wyoming's agricultural suitability standard for groundwater.

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