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Mobilization of Selenium from Coal Bed Methane (CBM) Produced Water Evaporation/Infiltration Impoundments in the Powder River Basin, Wyoming

Report by
Pedro 'Pete' Ramirez, Jr.
Environmental Contaminants Specialist
U.S. Fish & Wildlife Service
Cheyenne, Wyoming

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ABSTRACT

The development of coalbed methane (CBM) gas, a significant energy source, in the Powder River Basin (PRB) of northeastern Wyoming has also produced significant quantities of water requiring management and disposal. CBM produced water in the PRB is disposed of by direct discharge to: surface drainages, evaporation and infiltration impoundments, and, in a few cases, through irrigation. Six CBM infiltration impoundments with documented leakage and surfacing of water downstream of the impoundments were assessed for the mobilization and bioaccumulation of selenium. Carbon 13 ($\delta^{13}C$) analysis of water from four CBM infiltration ponds and downstream seeps indicate that water from three of the seeps is CBM water. Chemical analysis of water, soil/sediment, and biota (spiders) suggests the mobilization of selenium is occurring due to leaching of this trace element from the underlying strata. Waterborne selenium in four of the six CBM infiltration ponds and five of the six downstream seeps contained selenium above the 1.8 to 4.5 ug/L thresholds for exposure risks in freshwater environments (7 to 108 ug/L in the infiltration ponds and 25 to 356 ug/L in the downstream seeps. Spiders collected from two seeps had selenium concentrations of 13 and 46 ug/g, and exceeded the 2.8 ug/g dietary threshold for birds in a freshwater environment. CBM infiltration ponds supporting submerged aquatic vegetation and aquatic invertebrates could pose a selenium bioaccumulation risk to sensitive species of aquatic birds inhabiting these ponds. Although the downstream seeps are small and support minimal aquatic life (*e.g.* insects), extremely high levels of selenium are mobilized into the food chain. High concentrations of selenium in spiders collected in two of the seeps pose a risk to insectivorous songbirds. Consideration of infiltration ponds for CBM produced water disposal should be preceded by hydrogeological studies to determine if site conditions and the subsurface geology could result in the creation of contaminated groundwater plumes by the infiltration of the CBM produced water. The use of infiltration/evaporation ponds for the disposal of CBM produced water should be avoided if possible and other disposal options should be considered if there is potential for the mobilization of selenium and other trace elements.

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INTRODUCTION

The extraction of methane gas from coal seams is a significant energy source in the Powder River Basin (PRB) of northeastern Wyoming. Coalbed methane (CBM) gas is extracted by drilling wells into the coal seam and removing water to reduce the partial pressure and release the gas into the wellbore. Each CBM well produces an average of 10 gallons per minute (gpm) of water and a maximum of 100 gpm. CBM produced water is disposed of by direct discharge to surface drainages, passive treatment prior to surface discharge, discharge to upland and bottomland infiltration impoundments, discharge to containment impoundments, and deep-well injection. Untreated discharge to surface drainages is the primary method of disposal provided that the CBM produced water meets Wyoming water quality standards. CBM produced water is typically a sodium-bicarbonate type with total dissolved solids ranging from 200 to 4,000 mg/L and sodium-adsorption ratios (SAR) from 5.6 to 9 (Healy et. al. 2011). Elevated SAR in excess of 13 can cause adverse impacts to soils (Healy et. al. 2011, Soil Survey Laboratory 1995). Water that does not meet water quality standards due to elevated SAR cannot be discharged into surface drainages and is usually discharged into closed containment ponds for infiltration and evaporation.

CBM infiltration ponds can adversely impact the quality of groundwater by dissolving and mobilizing naturally occurring trace elements, such as selenium, and salts as the CBM produced water infiltrates the underlying geologic formations (Healy et. al. 2011). Healy et. al. (2011) documented elevated concentrations of selenium exceeding 300 ug/L in groundwater beneath a CBM infiltration pond and extending up to 198 meters (650 feet) downstream.

Selenium is of particular concern in the Powder River Basin as elevated concentrations could impact three sensitive fish species: the flathead chub (*Platygobio gracilis*), sturgeon chub (*Macrhybopsis gelida*), and the goldeye (*Hiodon alosoides*). Given its known impacts on sensitive species of fish (Lemly 2002), elevated selenium would likely compound the effects of existing threats to these species and could further limit their distributions in Wyoming. The BLM (2003) concluded that the infiltration of CBM produced water would likely “cause new springs and seeps to develop down gradient of locations where infiltration is occurring.” The Powder River reach from the confluence of Salt Creek downstream to the confluence with Clear Creek is listed as impaired by the Wyoming Department of Environmental Quality (2008) due to selenium. The Powder River is also listed as impaired due to chlorides from the confluence of Salt Creek downstream for an undetermined distance. Selenium surfacing at the downstream seeps could contribute to selenium loading of the Powder River depending on the proximity of seeps to the river and sufficient amounts of runoff flowing down the ephemeral drainages to transport the selenium into the river.

During periods of droughts, passerine songbirds and other wildlife are expected to use available water resources such as seeps downstream of CBM infiltration impoundments. Elevated selenium at these seeps could pose a risk to sensitive species of birds using these areas. According to Lemly (2002), selenium concentrations in water, sediment, and macroinvertebrates are considered a high bioaccumulation risk when the concentrations exceed 5 μg/L in water, 4 μg/g in sediment, and 5 μg/g in aquatic invertebrates. Selenium concentrations exceeding these concentrations can lead to dietary toxicity and reproductive failure in fish and aquatic birds (Lemly 2002). To gauge the potential risk of selenium-contaminated seeps from CBM infiltration/evaporation ponds to downstream aquatic communities and migratory birds this investigation was conducted in the Powder River breaks area in northeastern Wyoming (Figure 1). The objectives of this investigation were to determine:

- Selenium concentrations in water seeping downstream from the infiltration ponds;
- Selenium concentrations in bottom substrate within seep areas;
- Nature and extent of selenium contamination downstream of seep area; and
- Potential risk to downstream aquatic communities.

METHODS

The study area is located in the Powder River Basin of northeastern Wyoming (Figure 2). The Powder River breaks region consists of dissected plains and hills, terraces, and fans with some river breaks and badlands that formed in alluvium and colluvium from sandstone, shale, and siltstone (Nesser et.al. 1997). Elevations range from 2100 to 4980 feet. Drainage density is moderate to high. Water, sediment, and biota were collected from CBM infiltration seep sites in Johnson and Campbell counties, Wyoming (Table 1 and Figure 2). All sites, except the Maycock Ranch and Throne Ranch sites were located on public lands managed by the U.S. Bureau of Land Management. Permission to access the Maycock Ranch and Throne Ranch sites was obtained from the private land owners.

Each site included a separate sample of both water and sediment at the infiltration/ evaporation pond and the seep. Since the drainages upstream of the infiltration ponds were dry, soil samples instead of sediment were collected upstream of the infiltration ponds and submitted as reference samples. All soil and sediment samples were collected using a stainless steel spoon, placed into a stainless steel rectangular pan and transferred into Whirl-Pak® bags. All implements used in sample collections were washed with distilled water and rinsed with acetone before each use. Sediment samples were frozen immediately following collection.

Since aquatic organisms were not available in sufficient quantities for trace element analysis, spiders (*Schisocosa* spp) and insects from the Orders of Coleoptera, Hymentoptera, and Diptera (ants, beetles, and flies, respectively) were collected from the seep areas. Spiders can serve as a pathway for selenium and other trace elements in a terrestrial food web (Otter et.al. 2013, Rimmer et. al. 2010). Spiders were collected from the following CBM seeps: Maycock Ranch, Throne Ranch, Reservoir 49, and Reservoir 41. One composite sample of spiders was submitted for trace element analysis for each of these sites. Two composite samples of insects from the Maycock Ranch site and one from the Throne Ranch were submitted for trace element analysis.

Water samples from the CBM infiltration ponds and the downstream seeps were submitted to the University of Wyoming Stable Isotope Facility, Laramie, Wyoming for Carbon 13 ($\delta^{13}C$) analysis. Sharma and Frost (2008) report that the carbon isotope ^{13}C can be used to fingerprint water sources and differentiate CBM produced water from natural surface and groundwater. Water for $\delta^{13}C$ analysis was collected from the following locations in May 2012: Maycock Ranch, Throne Ranch, Reservoir 9, and Reservoir 41. The seeps at the Pat Reservoir and Pine Rock sites were dry in May 2012 and could not be sampled.

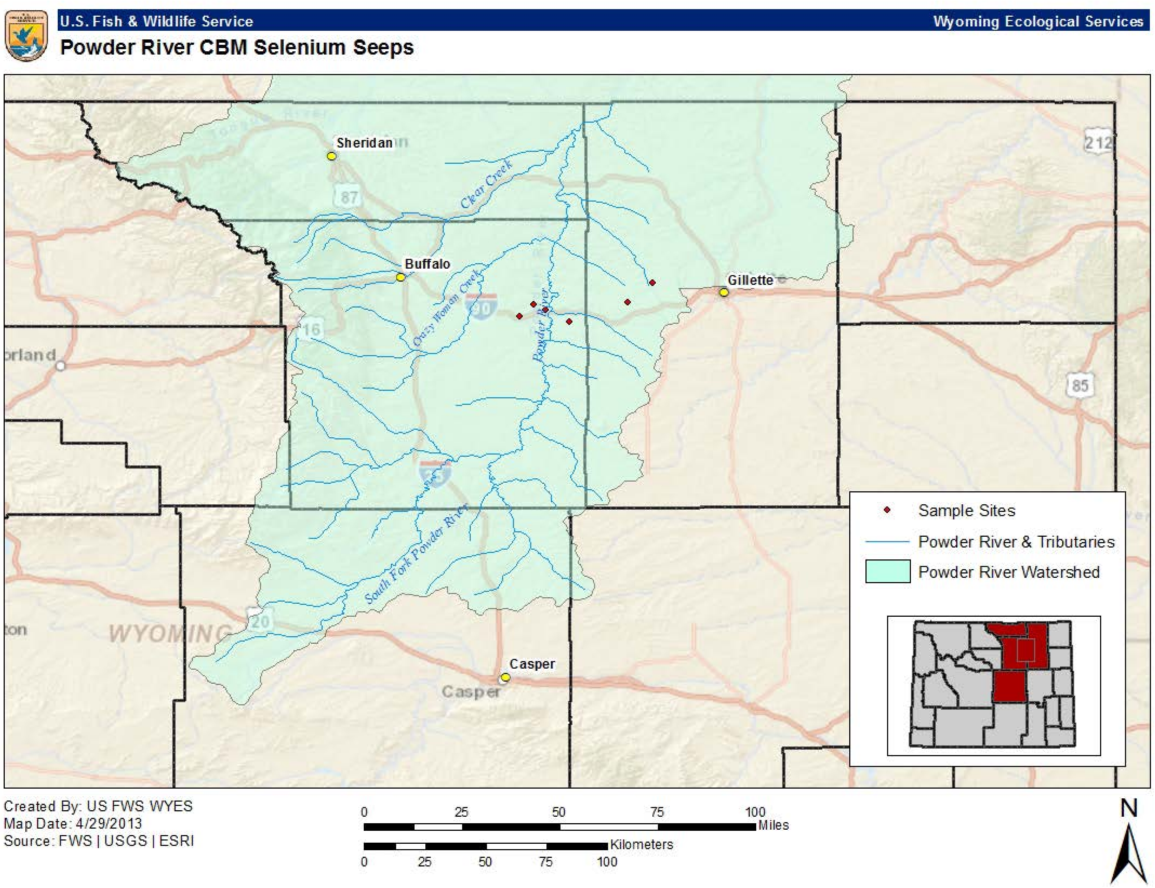

Figure 1. Location of the study area in the Powder River Basin, Wyoming.

Table 1. Locations of sampling sites in Johnson and Campbell Counties, Wyoming.

Site	Township	Range	Section	Quarter Section	Latitude Decimal Degrees	Longitude Decimal Degrees
Pat Reservoir	49N	78W	S20	SENE	44.2042582	-106.2616473
Reservoir 49	49N	78W	S2	NESW	44.242666	-106.18134
Reservoir 41	49N	77W	S18	NWNE	44.2256769	-106.1637656
Pine Rock	49N	76W	S36	NESW	44.182306	-106.074778
Maycock Ranch	49N	75W	S3	NENE	44.256681	-105.858161
Throne Ranch	50N	74W	S9	SWNW	44.325483	-105.769317

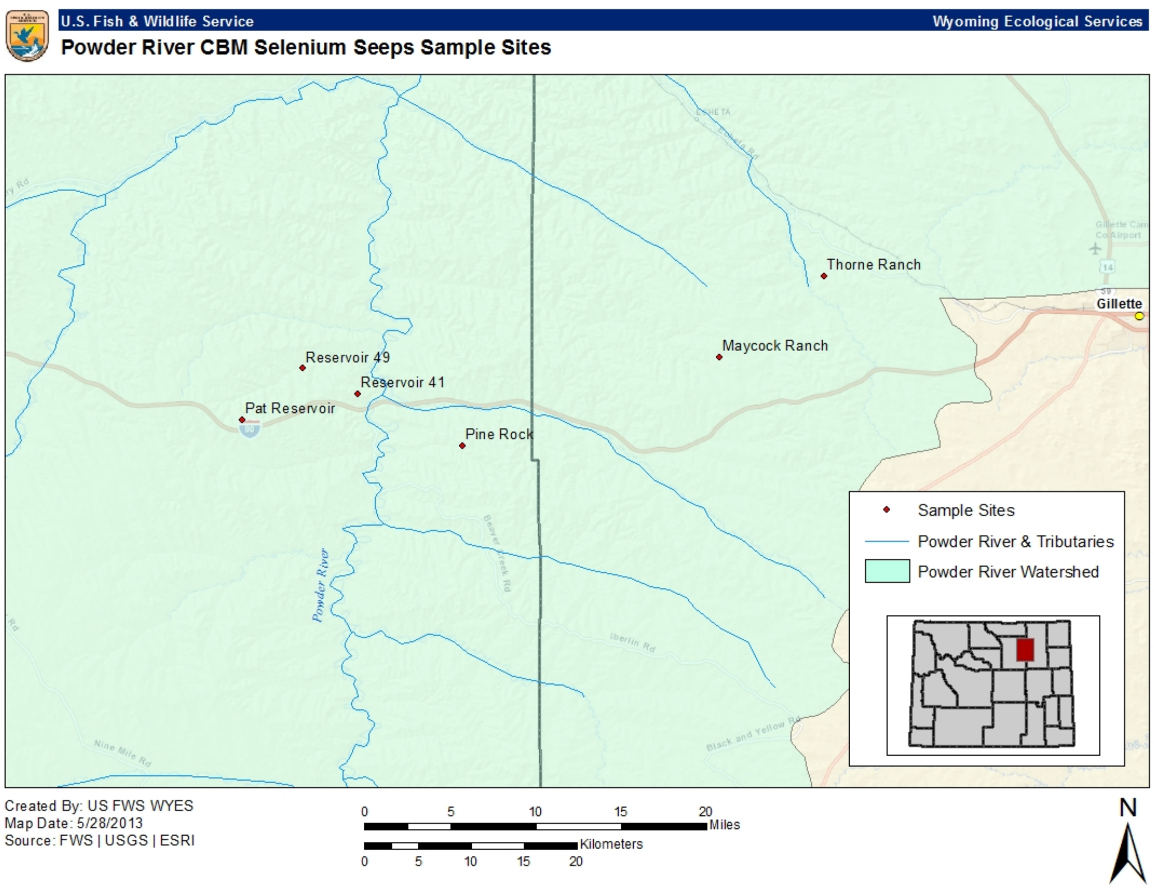

Figure 2. Location of sample sites in Johnson and Campbell Counties, Wyoming.

Water samples were collected in 1-liter chemically-clean polyethylene bottles with Teflon-lined lids. The pH in the water samples collected for trace element analyses was lowered to approximately 2.0 with laboratory grade nitric acid. Water samples for the other analytes were kept chilled in an ice-filled cooler and then transferred to a refrigerator (kept between 34°F and 38°F). Water, sediment, soil, and insect samples were submitted to the following laboratories under contract with the Service's Analytical Control Facility (ACF) at Shepherdstown, West Virginia, for analysis: Alpha Woods Hole Laboratories, Mansfield, Massachusetts; EnviroSystems, Inc., Hampton, New Hampshire; and Trace Element Research Laboratory, College Station, Texas. All samples were analyzed for trace elements. Arsenic, mercury, and selenium were analyzed using atomic absorption spectroscopy. Inductively Coupled Plasma Emission Spectroscopy was used to scan for a variety of elements including boron, barium, chromium, copper, lead, selenium, vanadium, and zinc. The ACF provided quality assurance and quality control for trace element analysis. Water was also analyzed by the Soil, Water and Plant Testing Laboratory at Colorado State University at Fort Collins, Colorado for total alkalinity, total dissolved solids, sulfates, chlorides, bicarbonates, calcium, total cations and total anions.

RESULTS

Waterborne selenium concentrations in the six CBM impoundments ranged from below detection to 108 ug/L (Table 2). Waterborne selenium concentrations in the seeps downstream of the CBM impoundments ranged from below detection limits in one seep to over 300 ug/L in three of the six seeps.

Table 2. Selenium concentrations (in ug/L) in water from CBM infiltration ponds and downstream seeps.

Location	Se (ug/L)	
	Pond	Seep
Maycock Ranch	< 5	25
Pine Rock	16.4	309
Reservoir 49	7	72
Throne Ranch	<5	<5
Reservoir 41	108	356
Pat Reservoir	8.5	309

Carbon 13 analysis of water from CBM infiltration ponds and downstream seeps indicate that water from the seep downstream of the Reservoir 49 CBM infiltration pond is CBM water (Table 3). CBM produced water typically has $\delta^{13}C$ values ranging from 12 parts per thousand (‰) to 22 ‰ and natural surface and groundwater have $\delta^{13}C$ values ranging from – 8 ‰ to – 11 ‰ (Sharma and Frost 2008). Water surfacing at the seeps downstream of both the Reservoir 41 and the Throne Ranch CBM infiltration ponds are a combination of CBM water and natural groundwater, while the seep at the Maycock Ranch is natural groundwater (C. Frost, University of Wyoming, Laramie, WY, personal communications, July 2, 2012).

Selenium concentrations in bottom substrate from the infiltration ponds and downstream seeps and in soil from reference sites immediately upstream of the infiltration ponds are shown in Table 4. With the exception of samples from the Throne Ranch site, selenium concentrations were higher in bottom substrate from the compared to concentrations in bottom substrate from the infiltration ponds and the reference soil samples. Selenium concentrations were highest in spiders collected from the seeps downstream of Reservoir 49 and Reservoir 41 (Table 5). Composite samples of insects collected at the Maycock Ranch and Throne Ranch sites did not contain elevated levels of selenium (Maycock Ranch 1.2 and 1.7 ug/g Se; Throne Ranch 0.99 ug/g Se).

Table 3. Carbon 13 ($\delta^{13}C$) analytical results for water from CBM infiltration ponds and downstream seeps.

Location	Site Type	$\delta^{13}C$	Water Source
Maycock Ranch	CBM Pond	10.8	CBM
Maycock Ranch	Downstream Seep	-12.7	Natural Groundwater
Throne Ranch	CBM Pond	-4.5	CBM & Natural Surface/Groundwater
Throne Ranch	Downstream Seep	-4.4	CBM & Natural Groundwater
Reservoir 49	CBM Pond	14.1	CBM
Reservoir 49	Downstream Seep	7.3	CBM
Reservoir 41	CBM Pond	12.7	CBM
Reservoir 41	Downstream Seep	-1.6	CBM & Natural Groundwater

Table 4. Selenium concentrations (in ug/g dry weight) in soil from reference sites and bottom substrate from CBM impoundments and downstream seeps.

Location	Se (ug/g dry wt)		
	Reference	Pond	Seep
Maycock Ranch	0.555	0.612	1.07
Pine Rock	0.394	4.43	7.82
Reservoir 49	0.298	0.787	5.08
Throne Ranch	0.892	0.316	0.53
Reservoir 41	0.626	2.88	4.17
Pat Reservoir	0.489	4.43	7.82

Table 5. Selenium concentrations (in ug/g dry wt) in spider composite samples.

Location	Se ug/g
Maycock Ranch	2.3
Reservoir 49	13.0
Throne Ranch	1.9
Reservoir 41	46.0

DISCUSSION

Although limited, the data suggest higher levels of selenium at the seeps may be due to leaching of this element from the subsurface soil and rock as the CBM produced water infiltrates and flows through these layers. Selenium was high in all but one of the seeps downstream of the CBM infiltration ponds. CBM produced is present in three out of the four seeps. Although the CBM produced water in the infiltration pond may be a source of selenium in the downstream seeps, additional selenium is probably also mobilized from the underlying strata. As evidence of this, waterborne selenium in the seeps in comparison to that of the upstream CBM infiltration pond, ranged from three times to three orders of magnitude higher. It is unlikely that the surface soils are the source of the selenium as concentrations in soils collected upstream of the infiltration ponds were low. Healy et. al. (2011) attributed selenium in groundwater underneath a CBM infiltration pond to pyrite in the unsaturated-zone sediments.

Water in four of the six CBM infiltration ponds contained selenium above the 1.8 to 4.5 ug/L thresholds for exposure risks identified for birds by Presser and Luoma (2010) in freshwater environments. One pond had waterborne selenium two orders of magnitude above the threshold. CBM infiltration ponds supporting submerged aquatic vegetation and aquatic invertebrates could pose a selenium bioaccumulation risk to sensitive species of aquatic birds inhabiting these ponds. Although the downstream seeps were small and supported minimal aquatic life (*e.g.* insects), extremely high levels of selenium were mobilized into the food chain. Elevated selenium concentrations in spiders collected in two of the seeps exceeded the 2.8 ug/g dietary threshold for birds in a freshwater environment (Presser and Luoma 2010). These selenium concentrations could pose a risk to insectivorous songbirds (Ohlendorf and Heinz 2012).

Although limited in scope, data from this study documents the mobilization of selenium at a localized level. The degree of risk depends on the timing and duration of use of these areas by sensitive species of wildlife and the extent to which less contaminated sites/prey are available to them. The transport of elevated selenium downstream to perennial streams inhabited by sensitive species of fish is unknown.

Selenium cycling at CBM infiltration impoundments and downstream seeps could persist for as long as CBM produced water is discharged into individual impoundments. In most cases, the volume of CBM produced water declines or ceases within 10 to 20 years of the life of the well (National Academy of Sciences 2010). Cessation of CBM produced water discharge more than likely will cause the downstream seeps to dry up as was the case with the Pine Rock and Pat Reservoir sites. However, the remaining earthen dams will impound water from precipitation events, which, depending on the volume, could reinitiate the selenium cycling.

MANAGEMENT RECOMMENDATIONS

Discharge of CBM produced water into infiltration impoundments constructed in ephemeral draws can result in the leaching of selenium from the underlying strata (Healy et. al. 2011) which can then enter into the food chain in downstream seeps where the water surfaces. Additionally, infiltration of CBM produced water can also mobilize large amounts of chloride and nitrate into the groundwater (Healy et. al. 2008, 2011). Disposal of CBM-produced water into closed containment ponds for infiltration and evaporation should be preceded by hydrogeological studies to determine if site conditions and the subsurface geology could result in the creation of selenium and or trace element-contaminated groundwater plumes downstream. The potential for the mobilization of selenium and other trace elements should also be assessed. Modeling of selenium exposure as described by Presser and Luoma (2010) should be conducted to better evaluate the risk of selenium exposure to migratory birds and other sensitive species of wildlife. The use of infiltration/ evaporation ponds for the disposal of CBM produced water should be avoided if possible and other disposal options should be considered.

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