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Establishing Appropriate Water Quality Numeric Standards under the Clean Water Act: Lessons from a Case Study of Coalbed Methane Produced Water Discharge to the Powder River, Wyoming and Montana

Carol D. Frost

Jason M. Mailloux

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ESTABLISHING APPROPRIATE WATER QUALITY NUMERIC STANDARDS UNDER THE CLEAN WATER ACT: LESSONS FROM A CASE STUDY OF COALBED METHANE PRODUCED WATER DISCHARGE TO THE POWDER RIVER, WYOMING AND MONTANA

*Carol D. Frost and Jason M. Mailloux**

* Carol Frost is a Professor of Geology and the Vice President of Special Projects at the University of Wyoming; Jason Mailloux is a Ph.D. candidate, Department of Geology and Geophysics, University of Wyoming. We would like to thank University of Wyoming Trustee David Palmerlee, Esq., for encouraging us to examine the administrative record of this case, and Brent R. Kunz, Hathaway & Kunz, and his staff for providing us the relevant documents.

I. INTRODUCTION

The Clean Water Act (CWA), passed in 1972, was intended to "restore and maintain the chemical, physical, and biological integrity of the Nation's waters."[1] The CWA regulates point source discharges of pollutants through a system of permits issued by the United States Environmental Protection Agency (EPA) or by state agencies authorized by the EPA.[2]

A dramatic growth in the recovery of coalbed methane (CBM) has taken place over the past decade in northeastern Wyoming. Concern over the effect of surface discharge of water produced with this natural gas led Montana to promulgate water quality standards under the CWA in 2003 and 2006 for rivers flowing from the area of production in Wyoming into Montana. Montana intended the regulations to address the possible impacts of CBM gas development on water quality in these watersheds.[3] The EPA approved Montana's regulations in 2003 and 2008, respectively.

Subsequently, four separate actions were filed (and later consolidated) seeking review of the EPA's approval of Montana's water quality standards.[4] In October 2009, the United States District Court for the District of Wyoming vacated the EPA's approval of Montana's 2003 and 2006 water quality standards and remanded the matter to the EPA with instructions to consider the 2003 administrative record and determine whether the 2003 numeric standards were based upon appropriate technical and scientific data.[5]

In a second ruling on discharge of CBM produced water announced in May 2010, the Montana Supreme Court ruled the Montana Department of Environmental Quality (MDEQ) violated the CWA and Montana's water quality act by permitting discharge of CBM produced waters without treatment.[6] The basis of the decision included the "highly saline" quality of the water that "may degrade the quality of the receiving surface waterway. Surface waters degraded

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[1] Clean Water Act of 1972, 33 U.S.C. § 1251(a) (2006).

[2] A point source refers to pollution that originates from a single, localized geographic area.

[3] Wyo. Dep't Envtl. Quality & Mont. Dep't Envtl. Quality, *Montana and Wyoming Powder River Interim Water Quality Criteria Memorandum of Cooperation* (Sept. 5, 2001), *available at* http://deq.mt.gov/CoalBedMethane/pdf/InterimWater.pdf; Notice of Public Hearing on Proposed Amendment and Adoption of Nondegradation Requirements for Electrical Conductivity (EC) and Sodium Adsorption Ratio (SAR), 19 Mont. Admin. Reg. 1844 (Oct. 6, 2005) [hereinafter Notice of Public Hearing on Proposed Amendment], *available at* http://sos.mt.gov/arm/register/archives/MAR2005/MAR0519.pdf.

[4] Pennaco Energy, Inc. v. EPA, 692 F. Supp. 2d 1297, 1299 (D. Wyo. 2009).

[5] *Id.* at 1315–16.

[6] N. Cheyenne Tribe v. Mont. Dep't Envtl. Quality, 234 P.3d 51, 58 (Mont. 2010).

by CBM discharge water, in turn, may have an adverse affect [sic] on irrigated agriculture and aquatic life."[7]

These rulings suggest uncertainty exists about the potential for CBM produced water to degrade surface water quality and the specific numeric standards necessary to protect surface water from potential degradation. It is important to develop standards that meet the intended purpose of protecting surface water from specific point sources of pollution and also withstand legal challenges. This article presents a case study illustrating how a collaborative approach between regulators and scientists is needed to accomplish these goals. First, this article reviews the EPA's administrative record from a scientific perspective, analyzing the scientific information used in a series of decisions that ultimately resulted in water quality standards. It then addresses the suitability of the standards adopted in this case study. Finally, this article recommends an improved process for future determinations of water quality standards under the CWA.

II. Background

The Powder River Basin (PRB) of northeastern Wyoming and southeastern Montana is one of the most significant energy-producing regions of the United States: PRB coal comprises approximately forty percent of all the coal produced in the nation annually.[8] These Tertiary-age, non-marine subbituminous coals are valued for their low sulfur and ash contents.[9]

PRB coals also contain a second fossil fuel resource: coalbed methane. Economically recoverable reserves in the Wyoming portion of the PRB are estimated at 23.2 trillion cubic feet, an amount approximately equal to ten to fifteen percent of the United States' natural gas reserve.[10] Production of this

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[7] *Id.* at 52.

[8] In 2008, the United States consumed 496 million short tons of PRB coal. U.S. Energy Info. Admin., Annual Coal Report (2010), *available at* http://www.eia.doe.gov/cneaf/coal/page/acr/acr.pdf.

[9] Non-marine coals are generally low in sulfur. Low sulfur coals are preferred as coal combustion releases sulfur in the form of SO_X, an air quality concern. The non-combustible product, called ash, requires disposal; coals with low ash contents are therefore desirable. Subbituminous is a grade of coal. Coal grades indicate the amount of energy contained per unit volume of coal. For a further discussion of coal, see generally Stanley P. Schweinfurth, U.S. Geological Survey, Coal—A Complex Natural Resource (USGS Circular 1143, 2003), *available at* http://pubs.usgs.gov/circ/c1143. Powder River Basin coals typically contain ~0.5% sulfur and 6–7% ash. M.S. Ellis et al., *Coal Resources, Powder River Basin*, *in* 1999 Resource Assessment of Selected Tertiary Coal Beds and Zones in the Northern Rocky Mountains and Great Plains Region tbls. PN-5 & -6 (USGS Prof'l Paper 1625-A, 1999), *available at* http://pubs.usgs.gov/pp/p1625a/Chapters/PN.pdf; R.M. Lyman & L.L. Hallberg, Wyoming Coal Mines and Markets 11 (USGS Rep. pt. CR-00-1, 2000).

[10] *See* Gregory C. Bank & Vello A. Kuuskraa, The Economics of Powder River Basin Coalbed Methane Development 2-4 tbl. 2 (Jan. 2006), *available at* http://fossil.energy.gov/programs/oilgas/publications/coalbed_methane/06_prb_study.pdf.

resource requires drilling a well to the target coal seam, typically less than 2000 feet, enlarging the hole diameter within the coal to create a large void, installing a submersible pump, and removing water from the coal seam. Water withdrawal reduces hydrostatic pressure in the coal seam, which allows the methane to desorb and rise up the annular space of the cased well.[11] After an initial period of water production, a typical well produces 175,000 cubic feet (4955 cubic meters) of methane per day and 3500 gallons (13,250 liters) of water per day.[12] Total production in the PRB is approximately 1.4 million cubic feet (~40,000 cubic meters) of methane per day, representing approximately seven percent of the total daily amount of natural gas produced in the United States.[13] Along with the gas, a total of 78.2 million gallons (296 million liters) of water are produced per day.[14] Over 1.85 trillion gallons (~7 trillion liters) of water are predicted to be produced over the approximately forty-five-year lifetime of the PRB development.[15]

The proper management of water produced with CBM is an important issue because this large volume of produced water has a chemical composition that may not be appropriate for all uses.[16] In some gas production areas, the produced water is re-injected into aquifers, but this is not a common management technique in the PRB of Wyoming and Montana due to cost. Most disposal methods in the PRB involve discharging produced water on the surface into surface drainages, into on- or off-channel impoundments, into the air by sprayers, or by using the produced water for surface and subsurface irrigation.[17]

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[11] RODNEY H. DEBRUIN ET AL., WYO. STATE GEOLOGICAL SURVEY, COALBED METHANE IN WYOMING (2004), *available at* http://www.wsgs.uwyo.edu/Publications/OnlinePubs/docs/coalbed.pdf.

[12] January 2009 data from the Wyoming Oil and Gas Conservation Commission. Carol D. Frost, Elizabeth L. Brinck, Jason M. Mailloux, Shikha Sharma, Catherine E. Campbell, Shaun A. Carter & Benjamin N. Pearson, *Innovative Approaches for Tracing Water Co-Produced with Coalbed Natural Gas: Applications of Strontium and Carbon Isotopes of Produced Water in the Powder River Basin, Wyoming and Montana*, *in* COALBED METHANE: ENERGY AND ENVIRONMENT 59–80 (Katta J. Reddy ed., 2010).

[13] *See* WYO. OIL & GAS CONSERVATION COMM'N, http://wogcc.state.wy.us (last visited Nov. 23, 2010); *Utah Energy and Mineral Statistics: U.S. Gross Withdrawals and Production of Natural Gas by State, 2001–2008*, ch. 4, tbl. 4.3a, http://geology.utah.gov/emp/energydata/natgasdata.htm (last updated Nov. 8, 2010).

[14] WYO. OIL & GAS CONSERVATION COMM'N, *supra* note 13.

[15] Elizabeth L. Brinck, James I. Drever & Carol D. Frost, *The Geochemical Evolution of Water Co-Produced with Coal Bed Natural Gas in the Powder River Basin, Wyoming*, 15 ENVTL. GEOSCIENCES 153, 154 (2008).

[16] For example, suitability for domestic, agricultural, or livestock use depends upon water quality, as described on the Wyoming Department of Environmental Quality website, available at http://deq.state.wy.us/wqd/WQDrules/Chapter_08.pdf.

[17] JOHN WHEATON & TERRY DONATO, MONT. BUREAU OF MINES & GEOLOGY, COALBED-METHANE BASICS: POWDER RIVER BASIN, INFORMATION PAMPHLET 5 (2004), *available at* http://www.mbmg.mtech.edu/pdf/ip_5.pdf.

Several river systems, including Rosebud Creek, and the Powder, Little Powder, and Tongue Rivers, traverse the CBM production area of the PRB and potentially may receive CBM produced water. It is these surface waters that the State of Montana intended to protect with its 2003 and 2006 water quality regulations.

III. DEVELOPMENT OF THE MONTANA RULES: A REVIEW OF THE ADMINISTRATIVE RECORD

As required by the CWA, the State of Montana adopted a nondegradation policy seeking to protect existing uses of surface water and limit the degradation of water quality.[18] In accordance with the CWA, Montana set numeric water quality standards and nondegradation requirements for the Tongue, Powder, and Little Powder watersheds.[19] In its approval of these standards on August 28, 2003, the EPA identified irrigated agriculture as the beneficial use most sensitive to development of CBM and the associated discharge of produced water.[20] The EPA also identified two principal constituents of concern in CBM produced water: salinity, measured by electrical conductivity (EC), and sodicity, measured by sodium adsorption ratio (SAR).[21] In 2006, the EPA's approval of the amended regulation confirmed both the designation of irrigated agriculture as the primary beneficial use to be protected and the choice of EC and SAR as the parameters by which water quality would be measured. The EPA approval document notes "[t]here is evidence in the record that EC and SAR may be harmful to plants and soils, and therefore harmful to irrigated agriculture, the most sensitive designated use for these two parameters in the Tongue River, Powder River and Little Powder River Basins."[22] The identification of irrigated agriculture as the beneficial use to be protected does not appear to have been a matter for discussion but instead

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[18] MONT. CODE ANN. § 75-5-303 (2010). Congress prohibits the discharge from a point source of any pollutant into the waters of the United States unless that discharge meets specific requirements set forth in the Clean Water Act. 33 U.S.C. § 1311(a) (2006). In order for point source discharges to be in compliance with the Act, such discharges must adhere to the terms of a National Pollutant Discharge Elimination System (NPDES) permit issued pursuant to the Act. *Id.* § 1342. Rather than vest the EPA with authority to control nonpoint source discharges through a permitting process, Congress required states to develop water quality standards for intrastate waters. *Id.* § 1313; Am. Wildlands v. Browner, 260 F.3d 1192, 1193–94 (10th Cir. 2001).

[19] Notice of Public Hearing on Proposed Amendment, *supra* note 3.

[20] Under the prior appropriation doctrine governing use of water in western states, water must be applied to a beneficial use. This term applies both to the purpose of use (e.g., irrigation, industrial, drinking water, etc.) and to the amount of water necessary to accomplish the purpose of the appropriation. Thus, Wyoming defines beneficial use as "the basis, the measure and limit of the right to use water . . . ." WYO. STAT. ANN. § 41-3-101 (2010).

[21] Pennaco Energy, Inc. v. EPA, 692 F. Supp. 2d 1297, 1303–04 (D. Wyo. 2009); *see infra* note 24 and accompanying text.

[22] *Pennaco Energy*, 692 F. Supp. 2d at 1306 (quoting the EPA Approval Document).

was taken for granted: the first document entered in the administrative record identifies native flora, and subsequent documents identify irrigated agriculture, as potentially sensitive to the effects of CBM produced water.[23]

A. *Water Quality Parameters for Ensuring Beneficial Use of Surface Water for Agriculture*

It appears no other water quality parameters other than salinity and sodicity were considered in the administrative record as appropriate measures of water quality to ensure beneficial use of surface water for agriculture.[24] As observed in the first document in the administrative record, salinity and sodicity affect plant health.[25] This document, authored by scientists at Montana State University-Bozeman, responds to questions regarding the tolerance and sensitivity of native and culturally significant plants on the Northern Cheyenne Reservation to possible increased salinity and sodicity associated with surface discharge of CBM produced water, along with the effects of flooding and changes in pH.[26] These authors note that different plants have varying tolerance for high salinity water, but in general high salinity can impact germination and the emergence and growth of seedling plants.[27] The study points out that sodicity is another important measure

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[23] The EPA administrative record is silent as to why irrigated agriculture was chosen as the area of primary concern. Nikos J. Warrance et al., *Salinity, Sodicity and Flooding Tolerance of Selected Plant Species of the Northern Cheyenne Reservation*, EPA Administrative Record at 1–36, Pennaco Energy, Inc. v. EPA, 692 F. Supp. 2d 1297 (D. Wyo. 2009) (Nos. 06-CV-100-B, 06-CV-229-B, 06-CV-235-B) (on file with author), *available at* http://waterquality.montana.edu/docs/methane/cheyenne.shtml (note the online source will have different pagination because, as cited, this document is part of a larger administrative record).

[24] Salinity is approximated by the electrical conductivity of water measured in µS/cm. Electrical conductivity (EC) increases as the concentration of ions in the solution, or total dissolved solids (TDS), increases. EC is related to TDS by the expression: TDS (mg/L) ~ 0.67 x EC at 25°C (µS/cm). *Electrical Conductivity (EC25) and TDS*, LAKE SUPERIOR / DULUTH STREAMS, http://www.lakesuperiorstreams.org/understanding/param_ec.html (last visited Nov. 23, 2010). SAR is a measure of the amount of sodium in water relative to magnesium and calcium. When units are in milliequivalents per liter, the equation for SAR is given by:

$$SAR = \frac{[Na^+]}{\left(\frac{[Ca^{2+}] + [Mg^{2+}]}{2}\right)^{1/2}}$$

WERNER STUMM & JAMES J. MORGAN, AQUATIC CHEMISTRY: CHEMICAL EQUILIBRIA AND RATES IN NATURAL WATERS 1040 (3d ed. 1996); ABE HORPESTAD ET AL., MONT. DEPT. OF ENVTL. QUALITY, WATER QUALITY TECHNICAL REPORT: WATER QUALITY IMPACTS FROM COAL BED METHANE DEVELOPMENT IN THE POWDER RIVER BASIN, WYOMING AND MONTANA (2001), EPA Administrative Record at 174, Pennaco Energy, Inc. v. EPA, 692 F. Supp. 2d 1297 (D. Wyo. 2009) (Nos. 06-CV-100-B, 06-CV-229-B, 06-CV-235-B) (on file with author), *available at* http://deq.mt.gov/coalbedmethane/CBMReports.mcpx (note the online source will have different pagination because, as cited, this document is part of a larger administrative record). Also identified in the report are threshold bicarbonate values that would protect fish in surface waters of the Powder River Basin. HORPESTAD ET AL., *supra*.

[25] Warrance et al., *supra* note 23 *passim*.

[26] Acidity is measured by: pH = -log [H^+].

[27] Warrance et al., *supra* note 23, at 17.

of the suitability of water for irrigation.[28] Irrigation with waters that are high in sodium relative to calcium and magnesium can degrade soil quality. The larger hydrated radius of sodium can cause the soil clay and organic matter to disperse and smectite clays to swell, reducing soil porosity, water infiltration, and root penetration.[29] It is important to note the potential impacts of SAR are less severe when the water is of higher salinity because a higher electrolyte concentration in soil solution reduces the effect of sodium-induced swelling and associated changes in soil structure.[30]

Other similar assessments are found within the EPA's administrative record, for example: "irrigated agriculture is expected to be the beneficial use most sensitive to the effects of CBM produced water and, for that use, the two principal CBM constituents of concern are SAR and salinity,"[31] and "because of the long history of use and data base in the literature, EC and SAR are likely to continue to be parameters of choice with which to evaluate water and soils for irrigation sustainability."[32] Accordingly, the EPA's administrative record shows that numeric pollutant concentrations for EC and SAR were selected because of the long-standing use of these parameters to assess agricultural water quality.

Because the impacts of SAR and EC are site specific, depending upon the specific soil, crops, and water management practices, there are no national numerical standards for these parameters. Instead safe thresholds must be set for each site.

B. Choice of Numerical Standards for EC and SAR

The only document in the administrative record that provides a basis for the numerical standards in the Montana regulations is a technical report created for the Montana Department of Environmental Quality (MDEQ).[33] These authors note the surface water in some watersheds in the PRB is relatively sodic and saline, such that if there was increased sodicity and salinity in these waters, continued use for irrigation could impact crop yields.[34] Figure 1 depicts the data

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[28] *Id.* at 7–8, 21.

[29] Elizabeth L. Brinck & Carol D. Frost, *Evaluation of Amendments Used to Prevent Sodification of Irrigated Fields*, 24 APPLIED GEOCHEMISTRY 2113, 2113 (2009).

[30] R.S. AYRES & D.W. WESTCOT, WATER QUALITY FOR AGRICULTURE, FAO IRRIGATION AND DRAINAGE PAPER 29 (1985), *available at* http://www.fao.org/docrep/003/t0234e/t0234e00.htm.

[31] HORPESTAD ET AL., *supra* note 24, at 174.

[32] Larry Munn, *Soil and Crop Issues for Irrigators on the Tongue River Related to Coal Bed Methane Product Water*, EPA Administrative Record at 303, Pennaco Energy, Inc. v. EPA, 692 F. Supp. 2d 1297 (D. Wyo. 2009) (Nos. 06-CV-100-B, 06-CV-229-B, 06-CV-235-B) (on file with author).

[33] HORPESTAD ET AL., *supra* note 24, at 174.

[34] *Id.* at 202.

from the technical report created for the MDEQ and shows a line indicating an approximate "irrigation threshold" above which crop yields may be lessened, the estimated water quality of CBM produced water in the Powder and Little Powder River watersheds, and the range and mean compositions of surface waters in the Powder and Little Powder Rivers taken from the historical record at United States Geological Survey (USGS) monitoring stations.

Figure 1

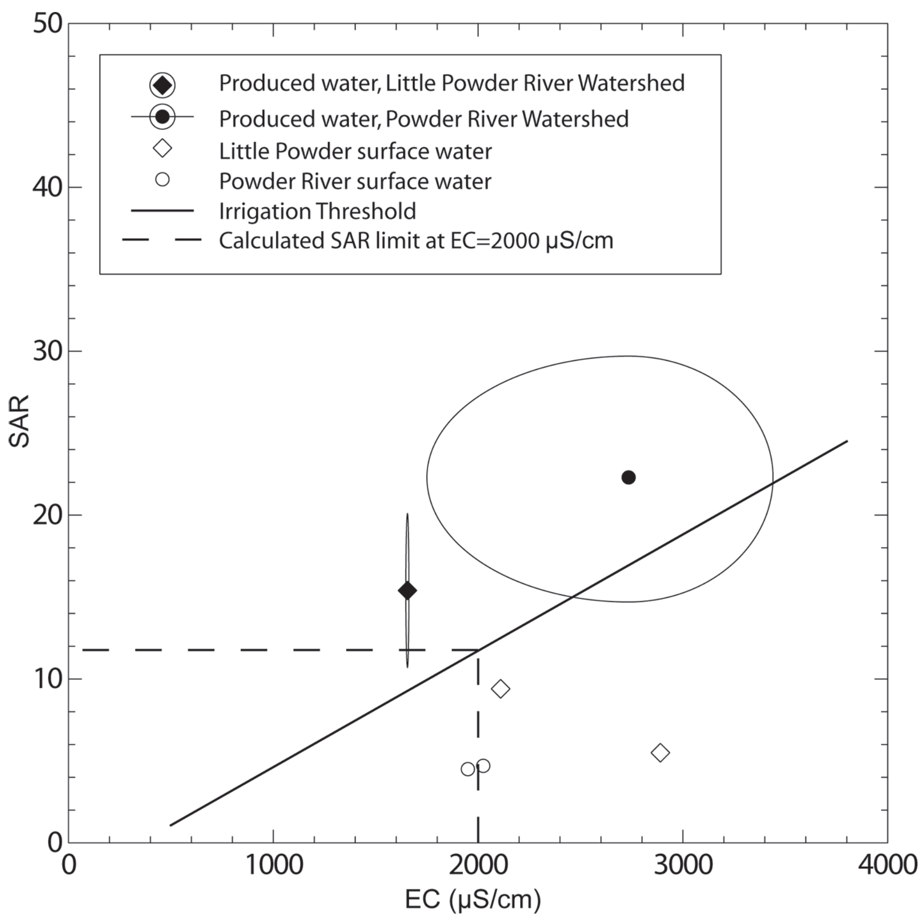

Figure 1. Plot of sodium adsorption ratio (SAR) against electrical conductivity (EC), showing values for Powder River water at Moorhead and Broadus and the Little Powder River near Weston and Broadus (open symbols). Also shown is the mean and range of CBM produced water from wells in the Powder and Little Powder watersheds (closed symbols and ellipses). The threshold value for SAR that corresponds to an EC of 2000 µS/cm is indicated by the dashed line. Data from HORPESTAD ET AL., *supra* note 24.

The water quality data for CBM produced waters from the technical report created for the MDEQ, shown in Figure 1, were derived from a report by O&G Environmental Consulting dated September 2001, a draft Environmental Impact Statement, and data provided by Fidelity Exploration.[35] Based on the potential number of CBM wells deemed by the Bureau of Land Management as "reasonably foreseeable development," modeling calculations were undertaken to estimate the effect on EC and SAR of discharging CBM produced water to surface water.[36] The proposed EC standard of 2000 μS/cm was based on current average surface water quality. As for the SAR standard, the technical report states, "[T]he SAR value calculated using the formula [SAR = 0.0071EC – 2.4754] is a reasonable estimate of an effect threshold."[37] By this expression, for an EC of 2000 μS/cm the SAR limit should be 11.7.[38] However, the Montana rules, which the EPA approved in 2003 and 2008, set the following standards: For the Powder River, the monthly average EC during the irrigation season (March 2 through October 31) must not exceed 2000 μS/cm with no sample above 2500 μS/cm, and the monthly average SAR must be 5.0 or less with no sample exceeding 7.5.[39] During the non-irrigation season (November 1 through March 1), the monthly average EC must not exceed 2500 μS/cm and no sample may exceed 2500 μS/cm.[40] The monthly average SAR must be 6.5 or less with no sample exceeding 9.75.[41] It is important to note that the average and maximum SAR standards, both during the irrigation season and during the rest of the year, are significantly below the 11.7 limit that is calculated using the guidelines of the technical report created for the MDEQ.[42]

It appears instead of using the relationship of SAR to EC as the basis for a SAR standard, the SAR numeric standards were chosen based upon sparse SAR data from surface water in the PRB available from USGS gauging stations. The Wyoming Department of Environmental Quality (WDEQ) made this observation in its response to the proposed numeric standards.[43] The WDEQ referred to publicly available USGS data collected in the years prior to CBM development. First, the WDEQ notes few SAR data are available from 1990 to 2001 at Moorhead,

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[35] *Id.* at 196. In general, data and interpretations from scientifically peer-reviewed sources are preferable to those relied upon for this technical report.

[36] *Id.* at 191.

[37] *Id.* at 184, 187.

[38] *See supra* Figure 1.

[39] MONT. DEP'T ENVTL. QUALITY, RECORD OF DECISION FOR MONTANA STATEWIDE OIL AND GAS ENVIRONMENTAL IMPACT STATEMENT 3 (Aug. 7, 2003), *available at* http://bogc.dnrc.state.mt.us/PDF/RODAug7_03.pdf.

[40] *Id.*

[41] *Id.*

[42] HORPESTAD ET AL., *supra* note 24, at 174–214.

[43] Letter from Dennis Hemmer, Dir., Wyo. Dep't of Envtl. Quality, to Jan Sensibaugh, Dir., Mont. Dep't of Envtl. Quality (Feb. 7, 2003) (on file with author).

Montana. "The available data indicates SAR levels near 5.0 for five months during the irrigation season; however, SAR levels for low flow periods (drought) were not available."[44] Second, the WDEQ stated, "USGS data for the Little Powder River near Weston, Wyoming indicated monthly SAR values during the irrigation season exceeding 5.0 for every month but April and September (4.95 and 4.19 respectively). In addition, monthly SAR values exceeded 7.5 for four of the twelve months."[45]

As was the case for EC, the SAR thresholds were apparently based upon measured surface water quality data. The monthly average SAR threshold of 5.0 or less was chosen to correspond to the limited SAR data that was available for the Powder River at the Moorhead, Montana USGS gauging station, neglecting evidence that natural SAR levels in other PRB river waters are typically higher than this threshold.

IV. Analysis: Evaluation of Rulemaking from a Scientific Perspective

Ample scientific evidence identifies EC and SAR as appropriate parameters for assessing the suitability of water for irrigation.[46] However, implicit in the MDEQ rules is the assumption that EC and SAR are appropriate parameters for identifying degradation caused by CBM produced water discharges to surface water. For this assumption to be valid, (1) EC and SAR values of ambient surface water and CBM produced water must be distinct; (2) the produced water must have higher EC and SAR values so that additions of produced water degrade surface water quality; and (3) no other processes can be responsible for increasing EC and SAR of surface waters. This section reviews published data for surface and CBM produced waters and evaluates these requirements.

A. EC and SAR of Ambient Surface Water and CBM Produced Water

A compilation of water quality data for CBM produced water and for the Powder River shown in Figure 2 reveals some striking differences in major ion chemistry for the two water sources.[47] Calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride

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[44] *Id.*

[45] *Id.*

[46] *See supra* Part III.A.

[47] *See* Catherine E. Campbell, Benjamin N. Pearson & Carol D. Frost, *Strontium Isotopes as Indicators of Aquifer Communication in an Area of Coal Bed Natural Gas Production, Powder River Basin, Wyoming and Montana*, 43 ROCKY MOUNTAIN GEOLOGY 149 (2008), *available at* http://faculty.gg.uwyo.edu/cfrost/pdfs/2008%20Campbell%20et%20al%20RMG.pdf; Benjamin N. Pearson, Sr. Isotope Ratio as a Monitor of Recharge and Aquifer Communication, Paleocene Fort Union Formation and Eocene Wasatch Formation, Powder River Basin, Wyoming and Montana (May 2002) (unpublished M.S. thesis, University of Wyoming) (on file with author) (containing water quality data); Scott A. Quillinan & Carol D. Frost, Spatial Variability of Coalbed Natural Gas Produced Water Quality, Powder River Basin: Implications for Future Development (Sept. 2010) (unpublished manuscript) (on file with author).

(Cl$^-$), and sulfate (SO_4^{2-}) are lower in CBM produced water, while iron ($Fe^{2+, 3+}$) and bicarbonate (HCO_3^-) are higher. SAR is quite variable in CBM produced water but is on average higher than in the Powder River. This is not because the produced water is particularly sodic but because it is low in calcium and magnesium. Total dissolved solids (TDS), the measure of salinity approximated by EC, is overlapping between produced water and Powder River water, but the produced water is on average less saline. This means that the addition of produced water to Powder River water is not likely to increase the salinity of the surface water, although SAR may increase.

Figure 2

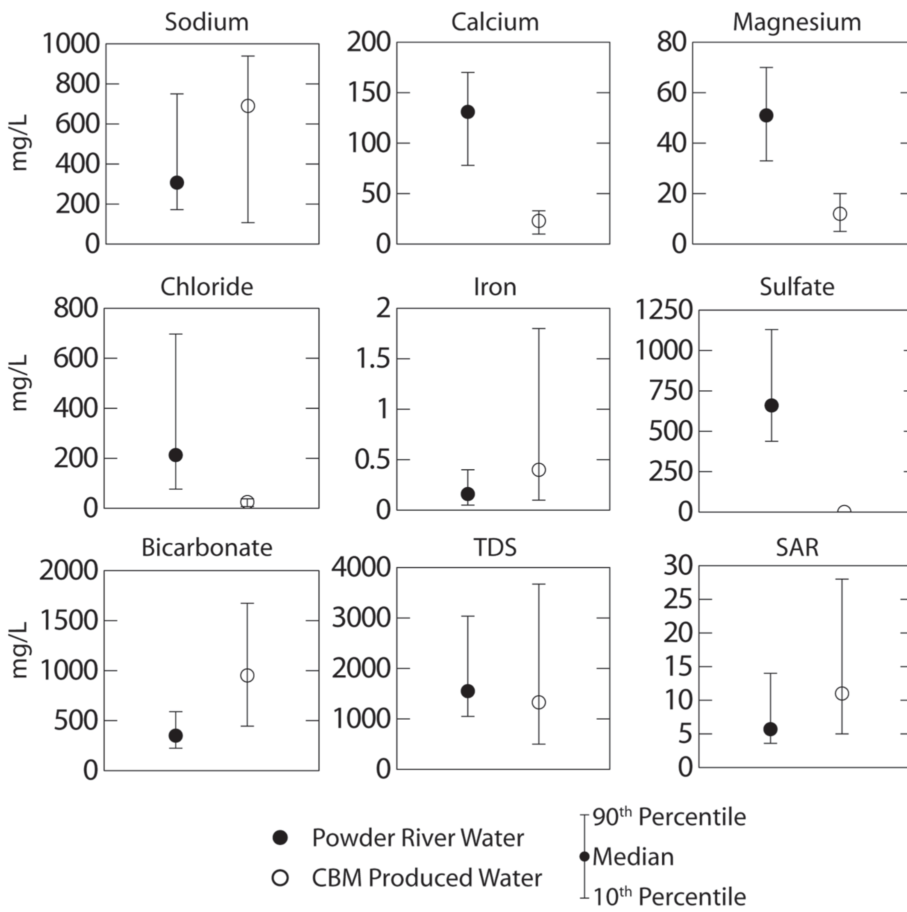

Figure 2. Major ion chemistry for the Powder River (closed circles) and CBM-produced water (open circles). Circles represent the median value; black bars represent the range between the tenth and ninetieth percentiles. TDS = total dissolved solids. For Powder River data, see U.S. GEOLOGICAL SURVEY, http://waterdata.usgs.gov/wy/nwis (last visited Nov. 22, 2010). For CBM data, see Campbell, Pearson & Frost, *supra* note 47; Pearson, *supra* note 47; Quillinan & Frost, *supra* note 47.

Examination of USGS gauging station data reveals significant spatial and temporal variations in water quality of surface waters in the PRB.[48] The water quality of CBM produced water also varies spatially.[49] To characterize the variations in Powder River water quality on a finer scale than is possible with a limited number of stream gauging stations, water samples were collected at thirty stations along the approximately 500-kilometer length of the Powder River (Figure 3).[50] The Powder River has a highly variable discharge; for this reason samples were collected both in the spring at high flow and in the fall at low flow. The discharge during the period of this study was as low as ~3 ft^3s^{-1} (0.085 m^3s^{-1}) at the low-flow period in the fall and over ~3500 ft^3s^{-1} (100 m^3s^{-1}) during the high-flow period associated with spring melt.[51]

Variations in EC and SAR are shown for low flow in Figure 4AB and for high flow in Figure 5AB. Also shown are the monthly average threshold (solid line) and the maximum limit at the time of sampling (dashed line) set by the Montana regulations for the irrigation season. The first five sample locations are along the north, middle, and south forks of the Powder River, as shown in Figure 3. The sample site at Sussex (Site 06 in Figure 3) is the first site along the main reach of the Powder River after the confluence of the three forks. Included among the sample stations are several tributaries farther downstream: marked by open circles are samples of Beaver Creek (Site 08, labeled BC in Figures 4 and 5), Flying E Creek (Site 11, labeled FEC in Figures 4 and 5), Crazy Woman Creek (Site 13, labeled CWC in Figures 4 and 5), and the Little Powder River (Site 24, labeled LPR in Figures 4 and 5). The flow in Beaver Creek and Flying E Creek is mainly due to discharge of CBM produced water. The area of major CBM production is indicated by the gray shading in Figures 4 and 5.

The fall 2007 samples from the Powder River (excluding tributaries) have EC that varies from 750 to nearly 3150 μS/cm, and in the spring, when the flow is augmented by dilute snowmelt waters, from 900 to 1900 μS/cm.[52] In most fall samples, the levels of EC exceed the Montana threshold for the irrigation season;

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[48] USGS WATER DATA FOR WYO., http://waterdata.usgs.gov/wy/nwis (last modified Nov. 24, 2010).

[49] Cynthia A. Rice et al., *Chemical and Isotopic Composition of Water in the Fort Union and Wasatch Formations of the Powder River Basin, Wyoming and Montana: Implications for Coalbed Methane Development*, *in* COALBED METHANE OF NORTH AMERICA II: THE ROCKY MOUNTAIN ASSOCIATION OF GEOLOGISTS 53 (2002); Campbell, Pearson & Frost, *supra* note 47 *passim.*

[50] *See* Jason M. Mailloux, Kiona Ogle & Carol D. Frost, *Application of a Bayesian Model to Infer the Amount of Coal Bed Natural Gas Produced Water in the Powder River, Wyoming and Montana*, *in* WATER RESOURCES RES. (forthcoming 2011); Shaun A. Carter, Geochemical Analysis of the Powder River, Wyoming/Montana and an Assessment of the Impacts of Coalbed Natural Gas Coproduced Water (2008) (unpublished M.S. thesis, University of Wyoming) (on file with author).

[51] USGS WATER DATA FOR WYO., *supra* note 48.

[52] Carter, *supra* note 50, at 147.

Figure 3

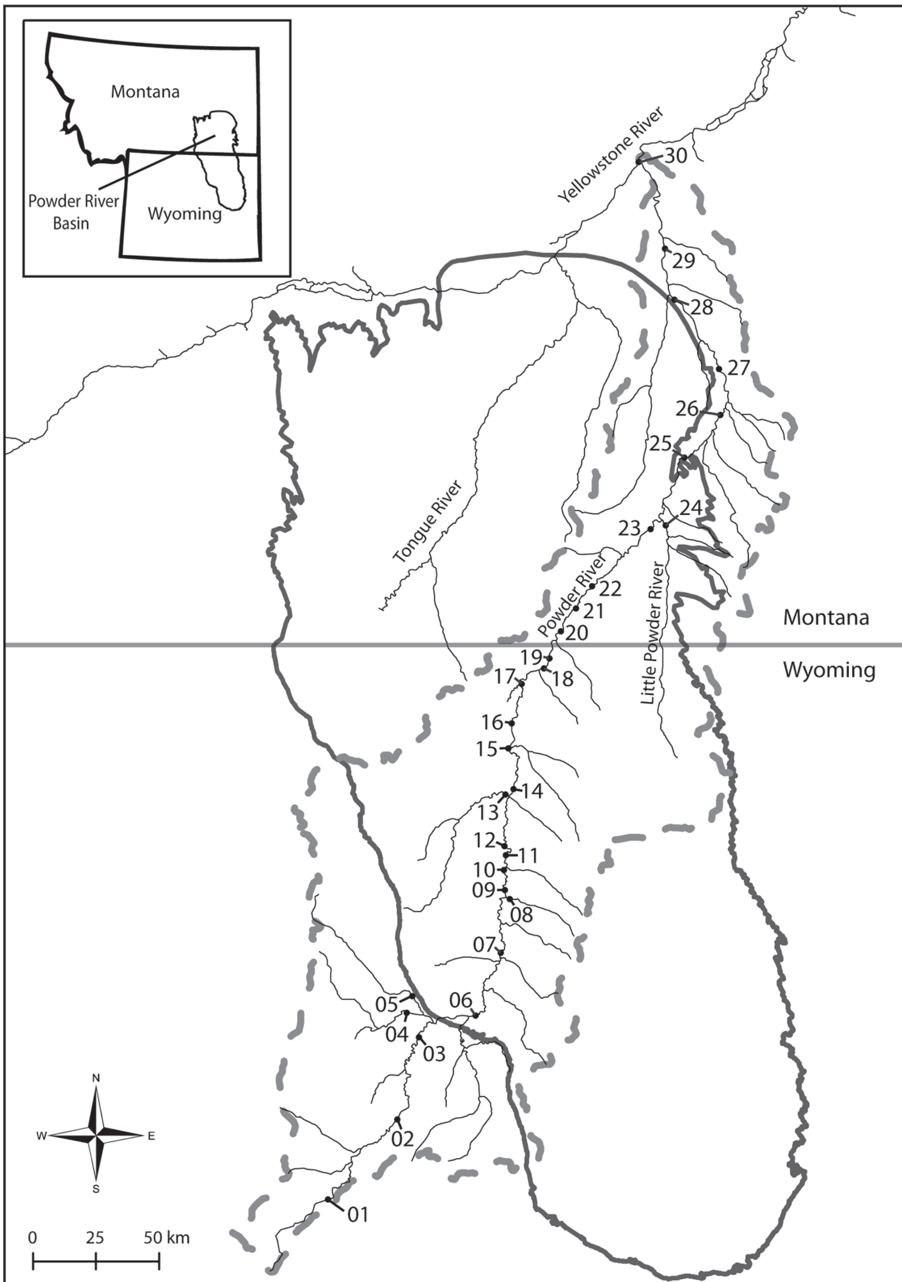

Figure 3. Map indicating the location of the Powder River basin (dark outline), the Powder River watershed (dashed line), and numbered sample sites along the Powder River. The main area of CBM development lies between Site 07 and the Montana/Wyoming state line.

Figure 4

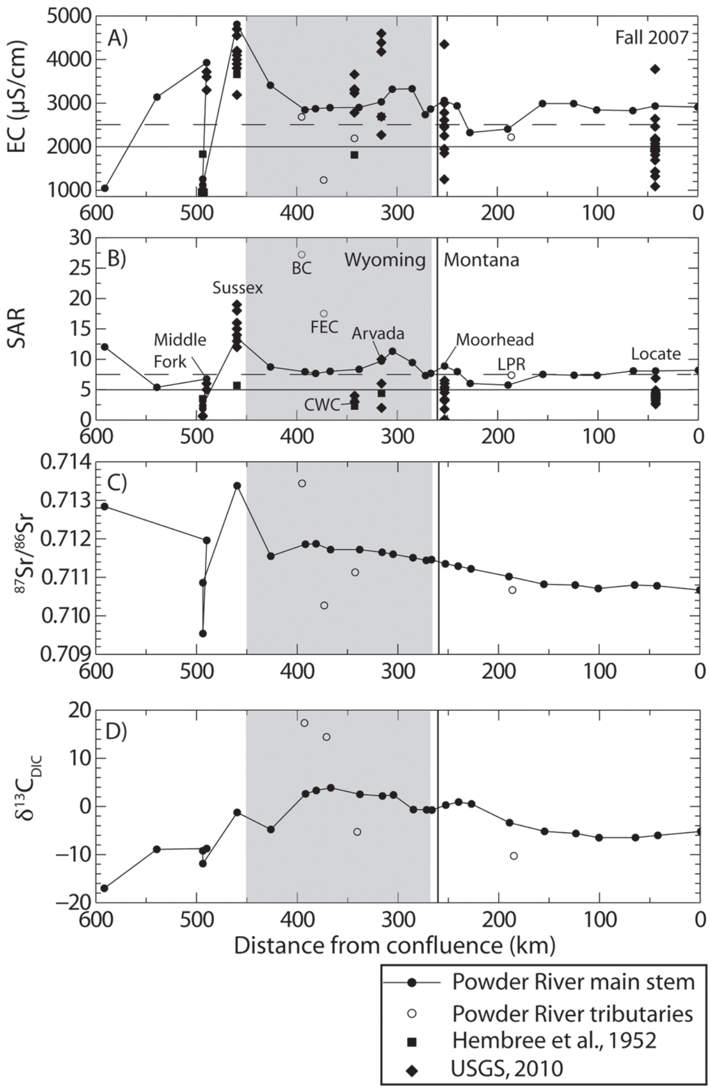

Figure 4. Water quality data collected in the fall of 2007. (A) Electrical conductivity (EC) of the Powder River plotted versus distance from the confluence with the Yellowstone River. The dashed line represents the Montana maximum limit for EC at the time of sampling (2500 μS/cm instantaneous); the solid line represents the average EC limit (2000 μS/cm). (B) Sodium adsorption ratio (SAR) of the Powder River plotted versus distance from the confluence with the Yellowstone River. The dashed line represents the Montana maximum limit for SAR at the time of sampling (7.5 instantaneous); the solid line represents the average SAR limit (5.0). (C) $^{87}Sr/^{86}Sr$ of the Powder River plotted versus distance from the confluence with the Yellowstone River. (D) $\delta^{13}C_{DIC}$ of the Powder River plotted versus distance from the confluence with the Yellowstone River. Tributaries are denoted by unfilled symbols (BC = Beaver Creek, FEC = Flying E Creek, CWC = Crazy Woman Creek, and LPR = Little Powder River).

Figure 5

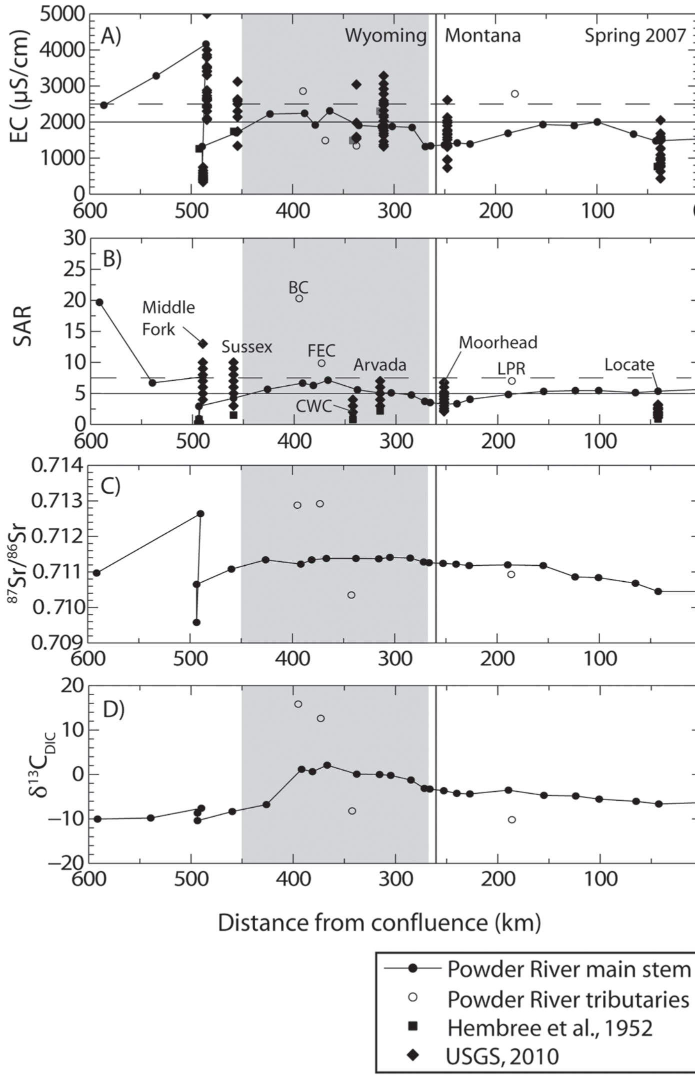

Figure 5. Water quality data collected in the spring of 2007. (A) Electrical conductivity (EC) of the Powder River plotted versus distance from the confluence with the Yellowstone River. The dashed line represents the Montana maximum limit for EC at the time of sampling (2500 µS/cm instantaneous); the solid line represents the average EC limit (2000 µS/cm). (B) Sodium adsorption ratio (SAR) of the Powder River plotted versus distance from the confluence with the Yellowstone River. The dashed line represents the Montana maximum limit for SAR at the time of sampling (7.5 instantaneous); the solid line represents the average SAR limit (5.0). (C) $^{87}Sr/^{86}Sr$ of the Powder River plotted versus distance from the confluence with the Yellowstone River. (D) $\delta^{13}C_{DIC}$ of the Powder River plotted versus distance from the confluence with the Yellowstone River. Tributaries are denoted by unfilled symbols (BC = Beaver Creek, FEC = Flying E Creek, CWC = Crazy Woman Creek, and LPR = Little Powder River).

in the spring, most samples are near the threshold. It is noteworthy that the EC of Beaver Creek and Flying E Creek are lower than the EC of water in the main stem of the river during low flow.

SAR for the Powder River also varies seasonally and along the length of the main stem of the river. SAR is highest during low flow (fall), when SAR ranged from 6.0 to 11.0. In the spring the SAR is lower, ranging from 4.0 to 10.0.[53] Almost all samples collected in fall 2007 exceed the Montana threshold for the irrigation season; samples collected in spring 2007 are near the threshold for the irrigation season.[54] The water samples from Beaver Creek and Flying E Creek have relatively high SAR because those tributaries are dominated by produced water.

The composition of CBM produced water also varies spatially across the PRB.[55] Near the recharge areas along the margins of the basin, the water within coal aquifers is relatively fresh (TDS < 100 mg/L) with low SAR (< 10.0). Farther in towards the center of the basin, the water becomes more saline (TDS > 3000 mg/L) and higher in SAR (20.0–40.0). Both EC and TDS are highest in the vicinity of the Powder River as it traverses the main CBM production area in northern Wyoming.

This summary of water quality data indicates: (1) EC and SAR are variable both in ambient surface water and in CBM produced water; (2) the EC values overlap but are on average lower in produced water; and (3) there is a large range of SAR measured in produced water and these SAR values are higher on average in produced water than in surface water.

B. Historical Water Quality Data

It is possible that the surface waters of Wyoming and Montana have already been affected by CBM produced water discharges such that their present-day EC and SAR have been altered from their historic values. We can evaluate this possibility in two ways: (1) by examining water quality data collected prior to coalbed methane development; and (2) by comparing values upstream of development to those from the main area of development. Historic data are plotted as solid diamonds in Figures 4 and 5.[56]

Comparing the EC values of modern and historic data, there is no obvious change in the salinity of the Powder River. Although EC upstream of development

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[53] *Id.*

[54] *See supra* notes 39–41 and accompanying text.

[55] Campbell, Pearson & Frost, *supra* note 47, at 155–59.

[56] CHARLES H. HEMBREE ET AL., SEDIMENTATION AND CHEMICAL QUALITY OF WATER IN THE POWDER RIVER DRAINAGE BASIN WYOMING AND MONTANA 92 (USGS Circular 170, 1952).

is highly variable and depends upon whether the tributaries are carrying dilute waters derived from snow and rain in the Bighorn Mountains or more saline waters with characteristics of drainages within the basin, there is no clear difference in EC upstream of development and locations farther downstream. This is expected because the EC of surface water and produced water overlap. If anything, the addition of produced water may dilute the salinity of surface water because produced water has on average lower TDS and therefore lower EC.

SAR data tell a different story. For a given location, the modern data tend to have higher SAR than the historic samples. An exception is at Sussex, where SAR is high in some of the historic data. This is likely due to the discharge of oil field brines associated with conventional oil and gas production at the Salt Creek oil field to the south. Produced water was discharged into Salt Creek until 1990, when the practice was reduced in favor of reinjection.[57] These discharges were found to increase the concentrations of sodium (Na^+), potassium (K^+), chloride (Cl^-), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}), while decreasing sulfate (SO_4^{2-}), calcium (Ca^{2+}), and magnesium (Mg^{2+}).[58]

C. *Other Processes that May Affect EC and SAR*

In the arid climate of the PRB, moisture is lost from surface waters by evaporation.[59] The potential effects of evaporation were evaluated by modeling the evaporation of typical Powder River water upstream of CBM development.[60] Evaporation increases the salinity of the remaining water. Moreover, as the water evaporates, calcium-bearing minerals such as calcite and aragonite precipitate from the water. This increases the SAR of the remaining water.

The effect of evaporation on SAR is illustrated with a few examples shown in Table 1. These calculations began with the composition of the Powder River

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[57] MELANIE L. CLARK ET AL., USGS MONITORING OF POWDER RIVER BASIN STREAM-WATER QUANTITY AND QUALITY (USGS Water Resources Investigations Rep. 01-4279, 2001), *available at* http://pubs.usgs.gov/wri/wri014279/pdf/wri014279.pdf.

[58] Ann M. Boelter et al., *Environmental Effects of Saline Oil-Field Discharges on Surface Waters*, 11 ENVTL. TOXICOLOGY & CHEMISTRY 1187 (1992).

[59] Aaron A. Payne & Demian M. Saffer, *Surface Water Hydrology and Shallow Groundwater Effects of Coalbed Natural Gas Development, Upper Beaver Creek Drainage, Powder River Basin, Wyoming*, *in Western Resources Project Final Report—Produced Groundwater Associated with Coalbed Natural Gas Production in the Powder River Basin*, 55 WYO. ST. GEOLOGICAL SURV. REP. OF INVESTIGATIONS 5, *available at* http://www.geosc.psu.edu/~dms45/CBM_report.pdf.

[60] Mailloux, Ogle & Frost, *supra* note 50. The potential effects of evaporation were evaluated by implementing a PHREEQC model to take typical Powder River water from upstream of CBM development and evaporate the water in increments of ten percent up to ninety percent. *Id.* As the water was evaporated, calcite and aragonite began to precipitate from the water with as little as ten percent evaporation for low-flow water chemistry. *Id.* SAR and EC increased in amounts similar or higher than is produced by mixing produced water with ambient Powder River water. *Id.*

sampled at Site 07, which is located immediately upstream of CBM development. Calculations were done using the composition of water at this site both in the fall, at low flow, and in the spring, at high flow. The change in EC and SAR that would result from ten percent and twenty percent evaporation of this water was calculated because evaporative losses of this magnitude have been measured in the PRB.[61] Inspection of Table 1 indicates EC and SAR increase as a result of evaporation. This underscores the point that EC and SAR may change in response to multiple processes, including by evaporation as well as through discharge of produced water into surface water. In fact, evaporation is the more likely process if both EC and SAR are observed to increase; because the EC of surface water and produced water are similar, addition of produced water to surface water should increase only SAR and affect EC very little.

Next, we compared the effects of evaporation on SAR and EC to the effect of mixing ten to twenty percent CBM produced water with Powder River water. Again we used the composition of water from Site 07 as representative of Powder River water. To this we added produced water, using the composition of water in Beaver Creek (Site 08) for the calculations. Table 1 shows that evaporation and mixing with produced water yield similar results for the composition of Powder River water at high flow, but that at low flow evaporation increases both EC and SAR to a greater degree than does mixing. In either case, the increases are modest compared to the seasonal variations in Powder River water composition at any given site: the differences in EC between water collected at high flow and at low flow may be over 1000 μS/cm and SAR varies by 3.0 or more.[62]

Table 1. Change in SAR and EC by evaporation or mixing with CBM produced water

	Evaporation		Mixing with CBM produced water	
ΔSAR	low flow	high flow	low flow	high flow
10%	2.2	0.8	0.6	1.0
20%	2.9	1.6	1.3	2.0
ΔEC (μS/cm)				
10%	230	57	25	63
20%	620	170	48	127

[61] Payne & Saffer, *supra* note 59, at 33–37.

[62] Carter, *supra* note 50.

Other observations from the data presented in Figures 4 and 5 suggest that CBM production in Wyoming cannot be the sole cause of EC and SAR that exceed the Montana thresholds. We note historic low flow EC measured many years prior to CBM production commonly exceeded the threshold value of 2500 μS/cm. Moreover, a rise in SAR north of the confluence with the Little Powder River cannot be related to Wyoming's energy industry because no streams entering the river north of the Little Powder have origins in Wyoming.

V. ALTERNATIVE APPROACHES TO IDENTIFYING COALBED PRODUCED WATER IN SURFACE WATERS OF THE POWDER RIVER BASIN

Several scientific studies demonstrate other, more viable tracers of CBM produced water than EC and SAR. These include stable isotopic compositions of naturally occurring strontium and dissolved inorganic carbon (DIC).[63] Strontium (Sr) is a useful environmental tracer because, unlike hydrogen and oxygen, its isotopes do not fractionate measurably in nature. The ratio $^{87}Sr/^{86}Sr$ provides a measurement of the relative proportion of radiogenic Sr-87 (formed by decay of rubidium-87) to primordial strontium, a ratio varying in natural materials depending on age and rubidium abundance. Groundwater obtains strontium from the dissolution of minerals or ion-exchange reactions on mineral and rock surfaces.[64] Differences in the $^{87}Sr/^{86}Sr$ ratio reflect natural variations of this ratio present in geologic materials. Measurements of the $^{87}Sr/^{86}Sr$ ratio are extremely precise (±0.00001), allowing very small differences in groundwater composition to be detected.[65] This precision enables the $^{87}Sr/^{86}Sr$ to be a valuable and effective tool to utilize for tracing the effects of CBM production in Wyoming as CBM produced water has a distinct $^{87}Sr/^{86}Sr$ relative to natural water sources. In the PRB, the $^{87}Sr/^{86}Sr$ of the produced water is more radiogenic ($^{87}Sr/^{86}Sr$ = 0.71268 to 0.71510) and more variable than the $^{87}Sr/^{86}Sr$ ratio from sandstone aquifers (0.71258 to 0.71271).[66] This explains the high $^{87}Sr/^{86}Sr$ ratio of water shown in Figures 4C and 5C for samples from Beaver Creek, which is composed almost entirely of CBM produced water.

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[63] Mailloux, Ogle & Frost, *supra* note 50, at 76–77; Carol D. Frost et al., *Sr Isotopic Tracing of Aquifer Interactions in an Area of Coal and Methane Production, Powder River Basin, Wyoming*, 30 GEOLOGY 923 (2002) [hereinafter *Sr Isotopic Tracing*]; Shikha Sharma & Carol D. Frost, *An Innovative Approach for Tracing Coal Bed Natural Gas Co-produced Water Using Stable Isotopes of Carbon and Hydrogen*, 46 GROUND WATER 329, 329–34 (2008), *available at* http://deq.mt.gov/coalbedmethane/cbm_water_quality.mcpx.

[64] *Sr Isotopic Tracing*, *supra* note 63, at 76–77.

[65] *Id.*

[66] Elizabeth L. Brink & Carol D. Frost, *Detecting Infiltration and Impacts of Introduced Water Using Strontium Isotopes*, 45 GROUND WATER 554 (2007); Campbell, Pearson & Frost, *supra* note 47, at 167–72; *Sr Isotopic Tracing*, *supra* note 63, at 76–77.

The ^{13}C composition of DIC ($\delta^{13}C_{DIC}$) also can be used to identify CBM produced water and trace its infiltration into ground water and streams.[67] CBM produced waters have a strongly positive $\delta^{13}C_{DIC}$ (12 to 22‰), which is easily distinguishable from the negative $\delta^{13}C_{DIC}$ of most surface and ground water (-11 to -8‰).[68] The elevated $\delta^{13}C_{DIC}$ in CBM produced water is explained by the preferential removal of ^{12}C by bacteria in an organic-rich system during microbial methane production, or methanogenesis. The continued preferential removal of the isotopically lighter molecules during methanogenesis results in a progressive shift in the remaining carbon pool towards heavier, ^{13}C-enriched values.[69] This process is responsible for the positive $\delta^{13}C_{DIC}$ of water shown in Figures 4D and 5D for samples from Beaver Creek and Flying E Creek, both of which carry CBM produced water to the Powder River. In fact, the positive $\delta^{13}C_{DIC}$ of the Powder River is a sensitive measure of the presence of produced water in the river water throughout much of northern Wyoming. $\delta^{13}C_{DIC}$ decreases north of the confluence of Clear Creek due to input from that tributary, which has not received produced water and has a flow comparable to the Powder River.

Produced water input into the Powder River can be quantified using $^{87}Sr/^{86}Sr$, $\delta^{13}C_{DIC}$, strontium, and DIC concentrations within a Bayesian statistical framework.[70] The authors determined that when the Powder River enters Montana, it is composed of at most ten to twenty percent CBM produced water, depending on the season and flow of the river. The calculations presented in Table 1 show the effect of this proportion of produced water on the composition of Powder River surface waters. The modest calculated increases in EC and SAR strongly suggest that the discharge of the current volume of produced waters is unlikely to raise EC and SAR enough to impact beneficial use of that surface water.

VI. SUMMARY AND RECOMMENDATIONS

A review of the EPA's administrative record reveals the determination of beneficial use and the choice of parameters to protect that use were established very early in the process of setting water quality standards. Reports included in the administrative record identify irrigated agriculture as the beneficial use most at risk from surface discharge of CBM produced water and recommended threshold values for two constituents, EC and SAR, to protect that beneficial use.[71] The

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[67] Sharma & Frost, *supra* note 63, at 332.

[68] Michael J. Whiticar, *Carbon and Hydrogen Isotope Systematics of Bacterial Formation and Oxidation of Methane*, 161 CHEMICAL GEOLOGY 291 (1999).

[69] *Id.*

[70] Mailloux, Ogle & Frost, *supra* note 50.

[71] HORPESTAD ET AL., *supra* note 24, at 12–13; Warrance et al., *supra* note 23, at 15.

technical report created for the MDEQ is the only document in the administrative record that undertakes a review of available water quality data and recommends numerical standards.[72]

EC and SAR are commonly used to assess the suitability of water for irrigation—hence they were a natural and immediate choice for Montana rule makers. However, at the time Montana proposed these rules, little data in the peer-reviewed literature on the chemical composition of CBM produced water existed, and this paucity may have led to the assumption that values of EC and SAR would be effective in identifying the presence of CBM produced water discharges to surface waters. The data used in the technical report created for the MDEQ were based upon a consultant's report; their reported mean, low, and high values for EC and SAR in the PRB are much higher than the values presented in Figure 2, which reflect a much greater number of analyses that have been published subsequent to the technical report created for the MDEQ.[73]

Although seasonal variations in stream *flow* were recognized in the technical report created for the MDEQ, the report did not address seasonal and spatial variations in surface water *quality*. Water quality data showing these variations were available at the time of the rulemaking from eight USGS gauging stations on the Powder River alone.[74] A subsequent, more detailed characterization of the Powder River clearly illustrates the magnitude of seasonal variations in water quality: during spring snowmelt the Powder River carries much more dilute water than in the fall when flow is lowest. Moreover, the composition varies along the length of the river.[75] Contributions from tributaries affect the water quality of the river downstream and in some instances dramatically change water composition; for example, Figures 4 and 5 show that EC drops markedly downstream of the confluence of the Powder River and Clear Creek. This variability complicates the identification of any water quality changes related to the input of CBM produced water, which, as shown by the calculations given above, produces only modest changes in EC and SAR.

Another complexity not reflected in the technical report created for the MDEQ is spatial variations in the composition of CBM produced water. As documented by workers at the University of Wyoming, produced water samples withdrawn from the margins of the PRB are quite dilute and commonly meet drinking water standards.[76] Additions of these produced waters to surface waters

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[72] HORPESTAD ET AL., *supra* note 24, at 12–13.

[73] *Id.*

[74] CLARK ET AL., *supra* note 57, at 2.

[75] Carter, *supra* note 50.

[76] Campbell, Pearson & Frost, *supra* note 47, at 154.

are unlikely to adversely affect its use for irrigation. On the other hand, produced water withdrawn near the center of the basin is much higher in SAR and EC and is of greater concern.

The spatial variations in CBM produced water quality along with the seasonal and spatial variations in surface water quality complicate the effective application of SAR and EC as parameters that monitor the degradation of surface water quality by discharge of CBM produced water. As shown in Figure 2, TDS of surface water and produced water overlap significantly, and the median SAR of each is similar. Table 1 shows changes in EC and SAR due to discharge of produced water into surface water are small compared to the compositional variability in these end-members. With the benefit of additional data and analysis published since Montana's original rulemaking, it is clear that these parameters are not optimal for identifying degradation due to input of produced water, and other potentially more effective parameters should be investigated.

Considering the lessons learned from this study, we recommend that future rulemaking would benefit from:

1. A comprehensive effort to collect and review all existing water quality data. In cases where such data are not published and accessible, as in the case of consultants' reports, the data tables should be reproduced and made available for review.

2. Involvement of researchers from state agencies, academic institutions, and industry. A collaborative effort involving discussion and brainstorming is more likely to develop alternative approaches to problems, to promote deliberation, and to produce creative solutions. Such discussions may also reveal knowledge gaps and stimulate additional data-gathering and research.

3. A charge to such a collaborative group to prepare a report of their work, including the data on which their recommendations are based, and several recommendations, each with an assessment of uncertainty.

VII. Conclusion

The CWA places the responsibility to protect surface waters on states, yet carrying out this responsibility is far from simple. Even if identifying the beneficial use most at risk from point-source pollutants is relatively clear-cut, choosing appropriate parameters and threshold values can be complex. In the case study examined in this article, spatial and temporal variations in water volumes and water quality of surface water in the PRB, along with spatial variations in the composition of CBM produced water, seriously complicate the effort to identify and quantify produced water discharged to the surface.

The brief review presented did not consider a number of other complexities, such as uncertainties in water volumes carried by tributaries, as well as conveyance loss in holding ponds and infiltration. Natural systems are temporally dynamic, changing seasonally.[77] Problems of this type will be most successfully addressed through the application of both conventional and innovative approaches. For example, strontium and carbon isotope measurements used within a Bayesian statistical modeling framework can estimate the contribution of CBM produced water to the Powder River during different seasons and flow conditions to determine the possible effects of CBM produced water on Powder River water quality. A comprehensive, collaborative effort on the part of researchers from state agencies, academia, and industry is required. Such a group should be charged with gathering all relevant data and with identifying multiple strategies and approaches that may potentially inform the problem. The group should then work together to fill data and knowledge gaps and to assess the strongest approaches and their likelihoods of success.

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[77] Payne & Saffer, *supra* note 59, at 62; Sharma & Frost, *supra* note 63, at 331–32; John Wheaton & Terry H. Brown, *Predicting Changes in Groundwater Quality Associated with Coalbed Natural Gas Infiltration Ponds*, *in Western Resources Project Final Report—Produced Groundwater Associated with Coalbed Natural Gas Production in the Powder River Basin*, WYO. ST. GEOLOGICAL SURV. (2005).