

Produced Water in the Western United States: Geographical Distribution, Occurrence, and Composition

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ABSTRACT

Coproduced water is a byproduct of oil and natural gas production. Because it is in contact with hydrocarbon products and geologic formations in underground basins, it usually contains elevated concentrations of inorganic and organic constituents. This paper aims to illustrate the concentration ranges for specific contaminants and the estimated quantity of coproduced water in the Western United States. The total dissolved solids (TDS) concentration in coproduced water can vary between 1,000 mg/L and over 400,000 mg/L; however, some basins tend to have much lower median values of TDS. Sodium chloride was found to be most dominant salt found in coproduced water across all basins studied. Oil and grease, ethyl benzene, benzene, phenols, and toluene are the most common organic contaminants found in coproduced water. The total oil content in coproduced water can range from 40 mg/L to 2,000 mg/L. Understanding the composition and quantity of coproduced water is essential for assessing the viability of beneficial reuse and selecting appropriate treatment processes for the water.

Key words: coproduced water; water quality; oil; natural gas; geographical distribution

INTRODUCTION

COPRODUCED WATER is defined as water that is extracted from subsurface geologic formations containing oil and gas (Society of Petroleum Engineers, N.D.). It is estimated that the oil and gas industry generates 10 times more water than oil and gas (Desalination and Water Purification Technology Roadmap, 2003). Current practice for disposal of coproduced water includes reinjection into underground formations, surface discharge into receiving waters, or land application. Reinjection is an expensive option for oil and gas producers and can only be done when the underground

structure can accommodate the water. Surface discharge can cause contamination of drinking water or irrigation water supplies either underground or on the surface. When applied to land, the excess salt commonly found in coproduced water can make soil less permeable to air and water and reduce the availability of nutrients in the soil (Veil *et al.*, 2004).

The estimated amount of coproduced water generated in the United States is between 6.1×10^6 m³/day and 7.8×10^6 m³/day (1,600 mg.day and 2,100 mg.day) (Boysen *et al.*, 2002; Veil *et al.*, 2004). This amount of water is greater than the combined daily water consumption for New York City and Los Angeles ("More Masses Huddling, 2006; Los

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Angeles Department of Water and Power, N.D.). In many areas of the United States, fresh water supplies have been fully allocated; therefore, additional sources of water must be identified to meet increasing water demands (Desalination and Water . . . , 2003). In the arid regions of the Western United States, treated coproduced water may relieve stresses on conventional water supplies and provide a stable source of water during times of drought (Veil *et al.*, 2004). Especially the Western U.S. is currently experiencing a significant growth of coproduced water production due to the increasing interest in exploring unconventional natural gas resources (coal bed methane, oil shale, and tight gas sands) to diversify the energy portfolio of the United States (Stevens *et al.*, 1998). Coal bed methane (CBM) accounts for 7% of the total natural gas production and 8% of the gas reserves in the United States. Development from the Rocky Mountain states of Colorado, New Mexico, Utah, and Wyoming accounts for nearly 8% of the total coalbed methane production in the United States (Bryner, 2006).

Understanding the chemical characteristics of coproduced water is important for determining appropriate treatment technologies and optimal beneficial uses of the water. Reactions between dissolved constituents in the water and interactions between the water and surrounding rocks or petroleum can affect the composition of coproduced water (Veil *et al.*, 2004). The inorganic chemical characteristics of coproduced water vary considerably depending on the geographic location and the geologic formation from which the petroleum and water were produced. The organic content of coproduced water depends heavily on the type of hydrocarbon produced and exists in two forms: suspended, dispersed oil droplets, and dissolved organic material (Stephensen, 1992).

The purpose of this study is to describe the current state of knowledge regarding the chemical characteristics of coproduced water from both conventional and nonconventional oil and gas, including the inorganic and organic content, along with the estimated volume of water available based on peer reviewed literature. Additionally, the scope of interest for this paper is the Western United States, including Montana, North Dakota, South Dakota, Wyoming, Utah, Colorado, Nebraska, Kansas, Arizona, New Mexico, Oklahoma, Texas, and California. The major oil and gas producing basins in the Western U.S. are Williston, Powder River, Big Horn, Wind River, Green River, Denver, Uinta-Piceance, Paradox, San Juan, Raton, Anadarko, Permian, San Joaquin, and Los Angeles (Energy Information Administration, 2004). A basin is a geographically confined depression in the earth's surface, consisting of layers of stratified rock, in which sediments accumulated and hydrocarbons may have formed (Van Dyke, 1997). This paper provides insight into the quantity and quality of coproduced water originating from these 14 basins.

CONVENTIONAL OIL AND GAS COPRODUCED WATER CHARACTERISTICS

Methodology

The U.S. Geological Survey (USGS) has published an extensive database containing the major ion analysis and total dissolved solids for water from 58,706 oil and gas wells (primarily from conventional oil and gas operations) from the mainland U.S., Alaska, and offshore (Breit and Otton, 2002). The database allows the user to download data by state or region. For this work, data were used from Montana, North Dakota, Wyoming, South Dakota, Utah, Colorado, Nebraska, Kansas, Arizona, New Mexico, Oklahoma, Texas, and California. There were 33,189 wells considered in this analysis (56.5% of the entries in the database where used). The geologic basin is provided for each well in the database. The data was reorganized by geologic basin, rather than by state. For some basins, the total dissolved solids (TDS) varied by geographical location and for these basins, the data was further organized by state within the basin. The minimum, median, first quartile, third quartile, and maximum values were calculated for each basin. Using the major ion analysis provided by the USGS database, milliequivalent concentrations were calculated for each ion. The anion and cation with the largest milliequivalent concentration was considered the dominant salt in the water.

A limitation of the USGS database is that it does not explicitly state which wells produce oil and which produce natural gas, the lifecycle of the wells, the flow rate of water from the well at the time of sampling, or the extraction technique used. Thus, the database is best used to draw general conclusions about the water generated by the petroleum industry as a whole.

Inorganic constituents

Coproduced water is generally characterized as brackish groundwater with elevated concentrations of total dissolved solids. The inorganic constituents present in coproduced water are primarily derived from the rock formations with which the water is in contact; therefore, the water quality regarding inorganic constituents is organized and presented by geologic basin. Water from conventional oil and gas can exhibit a wide range of TDS concentrations; 1,000 mg/L to over 400,000 mg/L. The TDS concentration range observed in coproduced water represented in the USGS database is presented in a box and whisker format with the minimum, first quartile, third quartile, and maximum value of TDS within each basin (Fig. 1). The data is presented on a log-scale to accommodate the large range of TDS values observed. For basins in which the TDS varied significantly, TDS statistics were calculated for each state occupied by the basin.

The Williston Basin exhibits the most geographical vari-

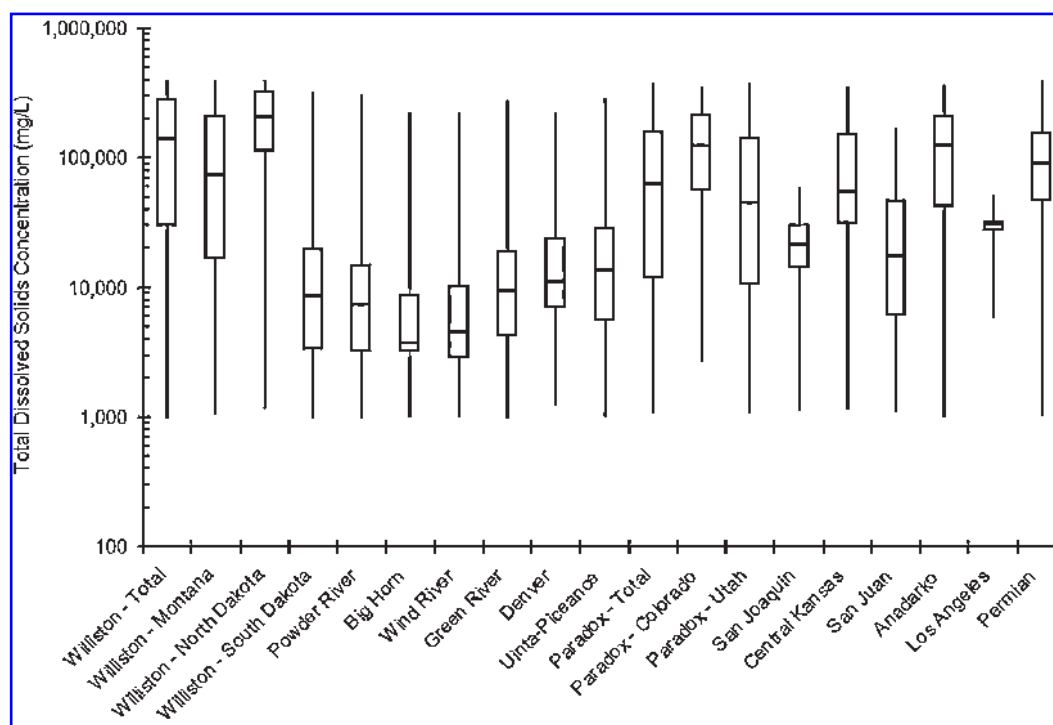


Figure 1. Distribution of TDS in produced water by basin. (Note: the outline of the box represents the 1st and 3rd quartiles, the bar in the box represents the median value, and the whisker length represents the minimum and maximum TDS values).

ation by state of any of the basins studied. The TDS of water samples within the Williston Basin are much higher for the portion of the basin that lies in North Dakota. Ranges of the most common inorganic constituents were obtained for all basins (Table 1). The TDS concentration ranged from 1,000 mg/L to 400,000 mg/L, with a median value of 32,300 mg/L for all basins. Sodium and chloride were the ions generally found in the highest concentrations.

Data was not available for arsenic, boron, and silica; however, these constituents are important to consider when using and treating the water because boron and arsenic are not removed by the majority of treatment processes and silica can cause scaling problems in membrane processes.

The USGS Produced Waters Database was used to compute the dominant salts present for each water sample analyzed. Sodium chloride was found to be the dominant salt in over 76% of the coproduced water samples. The next most common salts found in coproduced water are sodium bicarbonate and sodium sulfate (Fig. 2). Magnesium sulfate and magnesium chloride were found in a high concentration in the Big Horn Basin, Permian Basin, and Wind River Basin.

Organic contaminants

In contrast to the occurrence of inorganic constituents, which are determined by the geology of a basin, the quantity and characteristics of organic contaminants in copro-

duced water is impacted by a number of factors including type of hydrocarbon product the water is in contact with, volume of water production, artificial lift technique, and the age of production. To date, no studies have been conducted to quantify the impact of these factors on the organic content of coproduced water. The organic data presented here was derived from sources that reported on the organic content regardless of location and type of product. Table 2 lists the concentration ranges of organic material commonly found in coproduced water from oil and gas operations. Benzene, ethyl benzene, toluene, and phenol typically occur in the highest concentration in coproduced water (Table 2).

The data presented in Table 2 does not distinguish between water from oil operations and water from gas operations; however, water from gas production tends to have higher concentrations of low molecular-weight aromatic hydrocarbons, such as benzene, toluene, ethyl benzene, and xylene, than water from oil production (Jacobs *et al.*, 1992). Detectable concentrations of volatile organics are found in 75 to 80% of all gas coproduced water samples (Fillo *et al.*, 1992). Semi-volatile organics are rarely found in gas coproduced water and are much more prevalent in oil coproduced water.

Coproduced water occurrence

The amount of water generated during oil and gas extraction is not known exactly. Some states keep records of

Table 1. Ranges of common inorganic constituents in coproduced water.

Constituent	Units	Low	High	Median	Number of data points considered	Reference
TDS	mg/L	1000	400,000	32,300	33,189	Breit and Otton, 2002
Sodium	mg/L	ND	150,000	9,400	33,189	Breit and Otton, 2002
Chloride	mg/L	ND	250,000	29,000	33,189	Breit and Otton, 2002
Barium	mg/L	ND	850	Unknown	Unknown	Breit and Otton, 2002
Strontium	mg/L	ND	6,250	Unknown	Unknown	Breit and Otton, 2002
Sulfate	mg/L	ND	15,000	500	33,189	Breit and Otton, 2002
Bicarbonate	mg/L	ND	15,000	400	33,189	Breit and Otton, 2002
Calcium	mg/L	ND	74,000	1,500	33,189	Breit and Otton, 2002

Note: "unknown" in table signifies information not provided by the source.

coproduced water volumes, but for other states, estimates of water production are derived from oil/gas to water ratios. A number of different sources have provided estimates of coproduced water quantities (Boysen *et al.*, 2002; Veil *et al.*, 2004; Bryner, 2006); however, there is a large

variation in the water quantities reported. Where multiple values were obtained for water volume, the state reported figure was used preferentially. The oil/gas to water ratio was used only when a state figure was not available. The total amount of water generated in within the basins pre-

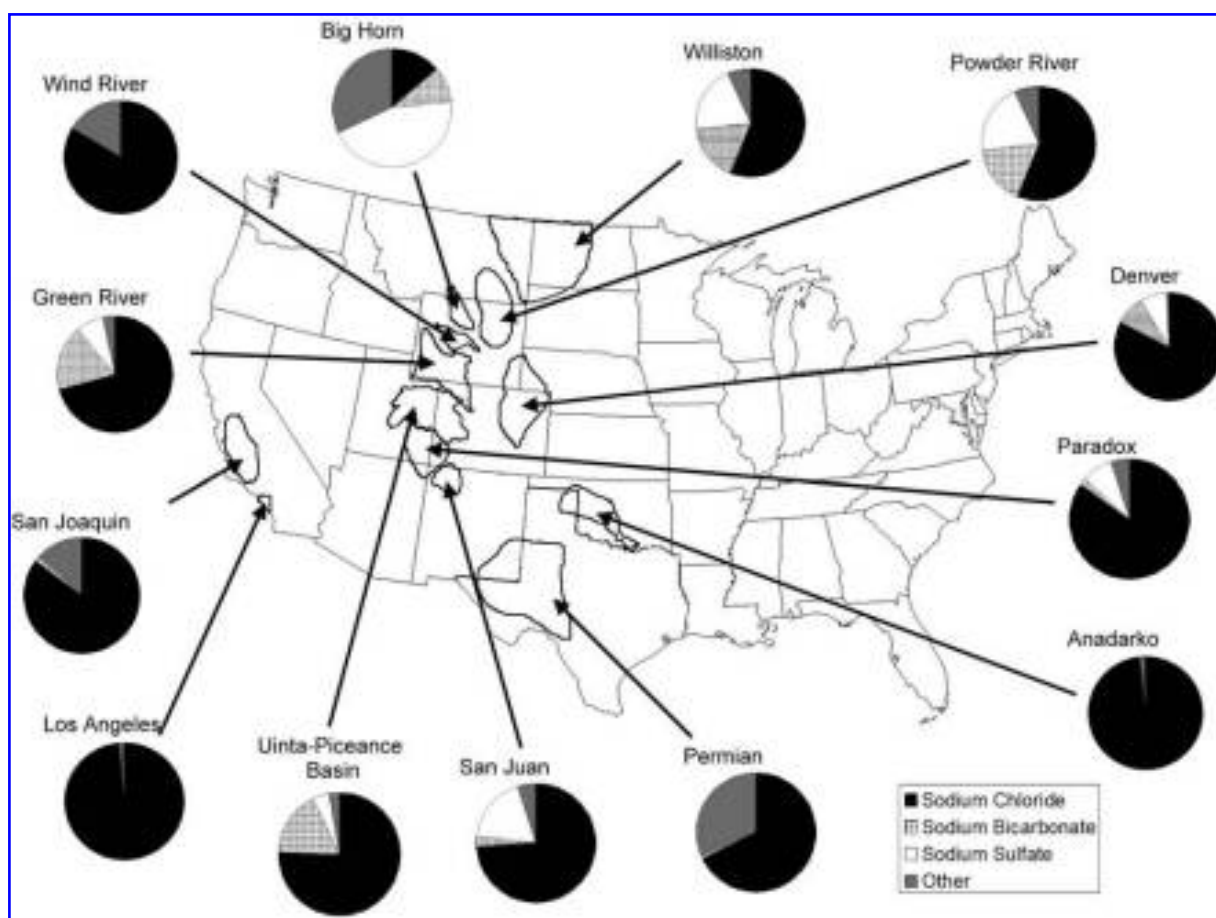
**Figure 2.** Dominant salts in produced water by geologic basin.

Table 2. Concentration ranges of organic material in coproduced water from conventional oil and gas.

<i>Constituent</i>	<i>Low</i>	<i>High</i>	<i>Median</i>	<i>Technique (method)</i>	<i>Reference</i>
TOC (mg/L)	ND	1,700	Unknown	UV Oxidation/IR (EPA 415.1)	Tibbetts et al. 1992
TSS (mg/L)	1.2	1,000	Unknown	Gravimetric (EPA 160.2)	Tibbetts et al. 1992
Total volatile organics (mg/L)	0.39	35	Unknown	GC/MS (EPA 1624 Rev B and EPA 24 & CLP)	Tibbetts et al. 1992
Total polar compounds (mg/L)	9.7	600	Unknown	Florisil column/IR	Tibbetts et al. 1992
Volatile fatty acids (mg/L)	2	4,900	Unknown	Direct GC/FID of water	Tibbetts et al. 1992
Total recoverable oil and grease (mg/L)	6.90	210.0	39.8	Unknown	Science Applications, 1994
2-Butanone (mg/L)	ND	0.37	Unknown	Unknown	Wesolowski et al., 1986
Benzene (mg/L)	ND	27	10	EPA Method 1624 and 624	Fillo et al., 1992
Benzoic acid (mg/L)	ND	13.5	3.80	Unknown	Science Applications, 1994
Bis (2-chlorethyl) ether (mg/L)	ND	0.03	Unknown	Unknown	Wesolowski et al., 1989
Ethyl benzene (mg/L)	ND	19	1.8	EPA Method 1624 and 624	Wesolowski et al., 1989
Hexanoic acid (mg/L)	ND	3.43	0.815	Unknown	Science Applications, 1994
Methylene Chloride (mg/L)	1.41	1.71	0.179	Unknown	Science Applications, 1994
<i>m</i> -xylene (mg/L)	0.015	0.611	0.137	Unknown	Science Applications, 1994
Naphthalene (mg/L)	ND	0.556	0.119	Unknown	Science Applications, 1994
N-decane (mg/L)	ND	0.797	0.116	Unknown	Science Applications, 1994
N-dodecane (mg/L)	ND	2.89	0.245	Unknown	Science Applications, 1994
N-hexadecane (mg/L)	ND	1.11	0.298	Unknown	Science Applications, 1994
N-octadecane (mg/L)	ND	0.246	0.106	Unknown	Science Applications, 1994
N-tetradecane (mg/L)	ND	0.404	0.138	Unknown	Science Applications, 1994
<i>p</i> -cresol (mg/L)	ND	0.541	0.123	Unknown	Science Applications, 1994
Phenol (mg/L)	0.009	23	NA	Silylation GC/MS	Tibbetts et al., 1992
Toluene (mg/L)	ND	37	9.7	EPA Method 1624 and 624	Fillo et al., 1992

ND, below detection limit; unknown, information was not provided by reference.

sented is estimated to vary from 106,000 m³/day (28 mgd) (Veil *et al.*, 2004) to over 1,197,000 m³/day (316 mgd) (Van Dyke, 1997). Water production data, median TDS value, and the potential for treatment was determined for each of the major producing basins in the Western United States (Table 3).

The potential for treatment within each basin was determined based on the median TDS concentration and the quantity of water within the basin, and is used as a preliminary assessment of where desalination treatment efforts should be focused on. Basins containing large quantities of water with relatively low TDS are considered to have more potential for treatment than basins producing small quantities with elevated TDS concentrations. Additional considerations impacting the potential for reuse, which were not considered in this study, are agricultural activity, stream flows, population centers, and logistical infrastructure (i.e., chemical supplies for water treatment processes) in proximity to the water production.

Table 3. Coproduced water generation by geologic basin.

<i>Geologic basin</i>	<i>Water production</i>		<i>Median TDS</i>	<i>Potential for</i>
	<i>m³/day</i>	<i>mg · day^a</i>	<i>(mg/L)^b</i>	<i>treatment</i>
Williston	18,000	4.9	132,400	Low
Powder River	370,000	97	7,300	Very high
Big Horn	360,000	94	4,900	Very high
Wind River	54,000	14	5,300	Very high
Green River	41,000	11	9,400	High
Denver	14,000	3.8	10,200	High
Uinta-Piceance	42,000	11	13,200	High
Paradox	21,000	5.6	67,000	Low
San Juan	14,000	3.6	22,700	Medium
Anadarko	34,000	8.9	132,200	Very low
Permian ^c	250,000	65	89,200	Low
San Joaquin	NA	NA	22,700	Medium
Los Angeles	NA	NA	30,330	Medium

^aBoysan et al, 2002; ^bBreit and Otton, 2002; ^cfor natural gas only and for the New Mexico portion of the Permian Basin.

Table 4. Total dissolved solids concentration for CBM producing basins.

<i>Basin</i>	<i>Units</i>	<i>Low</i>	<i>High</i>	<i>Mean</i>	<i>Number of data points considered</i>	<i>Reference</i>
Powder River	mg/L	370	1,940	840	47	^a
Uinta	mg/L	6,000	43,000	15,000	Unknown	^{b,c}
Piceance	mg/L	7,252	15,500	Unknown	Unknown	^d
San Juan	mg/L	10,434	23,464	Unknown	Unknown	^d
Raton	mg/L	1,100	4,600	1,500	Unknown	^{c,e}

Unknown, reference did not provide information; ^aRice, 2000; ^bHandbook, 2003; ^cHightower, ND; ^dMyers, 2005; ^eRaton Basin, 2003.

CBM COPRODUCED WATER CHARACTERISTICS

Methodology

Public domain and peer reviewed papers were used to gather data on the inorganic and organic constituents found in coal bed methane coproduced water.

Inorganic constituents

There are significant differences in the concentrations of major ions in coproduced water from CBM compared to conventional oil and gas. CBM generally produces water that has significantly lower TDS concentrations, ranging from 300 mg/L to 15,000 mg/L (Van Voast, 2003).

Water associated with CBM has a common chemical character: minimal sulfate, calcium, and magnesium, and larger quantities of sodium and bicarbonate (Van Voast, 2003). Based on the solubility of calcium and magnesium in the presence of bicarbonate, higher bicarbonate concentrations cause calcium and magnesium to precipitate, thus explaining their low concentrations in CBM coproduced water where bicarbonate is the dominant anion (Van Voast, 2003). There are five geologic basins that produce the majority of the CBM in the Western U.S.: Powder River, Uinta,

Piceance, Raton, and San Juan. The TDS range for CBM water generated in these basin is presented in Table 4. The concentration ranges of the common ions found in CBM water from the Powder River Basin are provided in Table 5.

Organic contaminants

The organic contaminants in water from CBM are derived from coal. CBM coproduced water generally has no oil and grease, and has relatively low dissolved organic carbon concentrations, usually varying from 2 mg/L to 10 mg/L (Kharaka and Rice, 2003). Some of the dissolved organic constituents known to be present in CBM water include goitrogens, such as 2-methyl resorcinol, 5-methylresorcinol, and hydroxypyridines. Polycyclic aromatic hydrocarbons, such as aminophenols and aromatic amines, are also known to leach into water from coals (Fisher and Santamaria, 2002). To the best knowledge of the authors, no studies have attempted yet to characterize dissolved organic constituents from CBM water.

Quantity of coproduced water

The quantity and quality of coproduced water in each basin was used to determine which basins are the most likely candidates for treatment of coproduced water toward bene-

Table 5. Ranges of common inorganic constituents in coproduced water from CBM in the Powder River Basin (Rice, 2000).

<i>Constituent</i>	<i>Units</i>	<i>Low</i>	<i>High</i>	<i>Mean</i>	<i>Number of data points considered</i>
Sodium	mg/L	130	800	300	47
Chloride	mg/L	6.3	64	13	47
Barium	mg/L	0.14	1.6	0.62	47
Strontium	mg/L	0.10	1.9	0.70	47
Sulfate	mg/L	ND	12	2.4	47
Bicarbonate	mg/L	290	2,320	950	47
Calcium	mg/L	5.9	57	32	47

Table 6. Coproduced water generation by geologic basin.

<i>Geologic basin</i>	<i>Water production</i>		<i>Median TDS (mg/L)</i>	<i>Potential for treatment</i>
	<i>m³/day</i>	<i>mg · day^a</i>		
Powder River	170,000	46	840	Very high
Uinta	19,000	5.1	15,000	Medium
San Juan	12,000	3.2	>10,000	High
Raton	13,000	3.6	1,500	High

^aRice and Nuccio, 2000.

ficial use. Basins exhibiting small TDS values and high water volumes were considered to have the most potential for reuse. The following values were compiled for water production from CBM producing basins (Rice and Nuccio, 2000) (Table 6).

QUALITY ASSURANCE

It is noteworthy that information regarding the makeup of coproduced water from both conventional and CBM exploration are associated with a fair degree of uncertainty. Although individual producers usually have a good understanding of quantity and quality of coproduced water from their operations, frequently this information is not readily available. Where possible, water quality parameters and water quantity estimates provided in this study were obtained from multiple sources. Additionally, these values were checked and found to be consistent with select complete water quality analyses from various coproduced water samples collected and analyzed by the authors.

SIGNIFICANCE OF WATER QUALITY AND QUANTITY TO TREATMENT

The analysis conducted in this study provides a starting point for determining what types of treatment strategies are appropriate for different types of coproduced water. Treatment technologies need to be tailored to the types and concentrations of constituents present in the water, the type of intended end-use, and the conditions under which the treatment will occur. Findings of this study illustrate that the TDS concentration of coproduced water might frequently be unsuitable for the desired end use of the water, and desalination technologies must be employed. Typical desalination technologies that have been used or proposed to treat coproduced water include reverse osmosis and nanofiltration, electrodialysis, capacitive deionization, ion exchange, chemical precipitation, and thermal or distillation processes, and hybrid combinations of these technologies. Some of

these technologies may not be capable in achieving the desired inorganic constituent removal efficiency or might exhibit limitations due to the presence of organic contaminants. Because many basins exhibit very similar water compositions, appropriate treatment process combinations are needed that meet the unique goals of coproduced water treatment, such as a high degree of robustness, high water recovery, little need for maintenance and treatment chemicals, minimal generation of treatment residuals, and ease of operation.

Attention should also be given to certain constituents present in the water that can be recovered and potentially sold as a product. In some cases, these products, such as iodide, can generate revenues that could cover the cost of the water treatment (Xu and Drewes, 2006). Currently, information is lacking regarding the concentrations of recoverable products within the basins targeted in this study; these constituents will need to be analyzed for on an individual basis.

CONCLUSIONS

Understanding the chemical composition and quantity of water available provides an idea of which areas of the Western U.S. have water most favorable for treatment, leading to beneficial use. Nearly all of the water qualities presented would require at least minimal organics removal and desalination to render it for beneficial use. Because the majority of coproduced waters exhibits a rather homogeneous composition of major ions, such as sodium, chloride, sulfate, and bicarbonate, desalination technologies that are already well established in the water industry like reverse osmosis, nanofiltration, or electrodialysis or combinations of these processes could assure a treated water quality that meets nonpotable and potable standards. However, some of the basins presented here have water with such high TDS concentrations that treatment will most likely not be cost effective. For these basins, treatment for beneficial use is not practical, and other options need to be investigated for disposal. Future research should be directed toward the development of robust, low-maintenance, easy to operate, package treatment technologies that can be employed at the wellhead or well clusters of oil and gas production sites.

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