International Journal of Coal Geology 126 (2014) 162–170

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

Surface disposal of produced waters in western and southwestern Pennsylvania: Potential for accumulation of alkali-earth elements in sediments

Katherine J. Skalak [a,*], Mark A. Engle [a,b], Elisabeth L. Rowan [a], Glenn D. Jolly [a], Kathryn M. Conko [a], Adam J. Benthem [a], Thomas F. Kraemer [c]

[a] U.S. Geological Survey, Reston, VA, United States
[b] Dept. of Geological Sciences, University of Texas at El Paso, El Paso, TX, United States
[c] U.S. Geological Survey, Woods Hole, MA, United States

ARTICLE INFO

Article history:
Received 27 June 2013
Received in revised form 2 December 2013
Accepted 2 December 2013
Available online 12 December 2013

Keywords:
Produced waters disposal
Sediment contaminant
Environmental impact
Unconventional gas extraction
Conventional gas extraction

ABSTRACT

Waters co-produced with hydrocarbons in the Appalachian Basin are of notably poor quality (concentrations of total dissolved solids (TDS) and total radium up to and exceeding 300,000 mg/L and 10,000 pCi/L, respectively). Since 2008, a rapid increase in Marcellus Shale gas production has led to a commensurate rise in associated wastewater while generation of produced water from conventional oil and gas activities has continued. In this study, we assess whether disposal practices from treatment of produced waters from both shale gas and conventional operations in Pennsylvania could result in the accumulation of associated alkali earth elements. The results from our 5 study sites indicate that there was no increase in concentrations of total Ra (Ra-226) and extractable Ba, Ca, Na, or Sr in fluvial sediments downstream of the discharge outfalls ($p > 0.05$) of publicly owned treatment works (POTWs) and centralized waste treatment facilities (CWTs). However, the use of road spreading of brines from conventional oil and gas wells for deicing resulted in accumulation of Ra-226 (1.2×), and extractable Sr (3.0×), Ca (5.3×), and Na (6.2×) in soil and sediment proximal to roads ($p < 0.05$). Although this study is an important initial assessment of the impacts of these disposal practices, more work is needed to consider the environmental consequences of produced waters management.

Published by Elsevier B.V.

1. Introduction

Significant volumes of water are co-produced with petroleum products and if not properly handled, present a potential source of contamination to the environment. The Appalachian Basin of the eastern United States and Canada produces brines of notably poor quality with TDS concentrations up to and exceeding 300,000 mg/L and total radium (Ra) > 10,000 pCi/L (Dresel and Rose, 2010; Rowan et al., 2011). Produced water volumes have increased nearly exponentially since 2005 with the development of the Middle Devonian Marcellus Shale (Soeder and Kappel, 2009). Proper management of the increased volumes of produced water from the Marcellus, along with conventional oil and gas plays within the basin has been a significant challenge for both the industry and regulators (Wilson and VanBriesen, 2012).

In the case of conventional oil and gas wells, formation brines present in the hydrocarbon reservoirs comprise the vast majority of the produced water. These fluids are well characterized in the Appalachian Basin; a data compilation of geochemistry of produced waters from conventional Devonian age reservoirs in Pennsylvania and West Virginia (see Engle and Rowan (2014-this volume) for details, n = 92 samples) shows that these fluids, which originated as highly evaporated paleoseawater, exhibit high salinities (geometric mean = 165 g/L, maximum 345 g/L) and elevated concentrations of some alkali earth metals (geometric means = 14,200 mg calcium (Ca)/L; 248 mg strontium (Sr)/L; and 24 mg barium (Ba)/L; maximum values = 38,400 mg Ca/L; 13,100 mg Sr/L; and 4370 mg Ba/L). By comparison, produced waters from the Marcellus Shale in the early stages of fracturing, which represents mixtures of the injected hydraulic fracturing fluid and formation brine, contain slightly lower total dissolved solids (geometric mean = 25.3 g/L), owing to mixing with the less saline fracturing fluid. However, late stage produced waters from Marcellus Shale gas wells tend to exhibit slightly enriched concentrations of Sr, Ba, and Ra relative to the conventional wells from adjacent reservoirs (Engle and Rowan, 2014-this volume; Rowan et al., 2011). For instance, samples of produced fluid from day 90 of production from nine Marcellus Shale gas wells across Pennsylvania and West Virginia exhibit geometric means of 3220 mg Sr/L and 809 mg Ba/L and maximum values of 8460 mg Sr/L and 4370 mg Ba/L (Hayes, 2009). Similarly, a compilation of historical and new Ra-226 and Ra-228 activity data for produced waters in the northern Appalachian Basin

* Corresponding author at. 430 National Center, U.S. Geological Survey, Reston, VA 20192.
E-mail address: kskalak@usgs.gov (K.J. Skalak).

0166-5162/$ – see front matter. Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.coal.2013.12.001

showed that while produced waters in general are enriched in Ra, those from the Marcellus are ~2–5 times higher than conventional oil and gas wells for a given salinity (Rowan et al., 2011). While the origin of the alkali earth elements in the produced waters is outside the scope of this current effort, their apparent enrichment in produced waters from the Appalachian Basin presents challenges for disposal.

There are five basic approaches to manage wastewater generated during the production of hydrocarbons: 1) minimization of produced water generation, 2) recycling and reuse within gas drilling operations, 3) treatment, 4) disposal, and 5) beneficial reuse outside of operations. Minimization, recycling, and reuse are used mostly for water produced early in shale gas operations (also called flowback), when salinity tends to be lower; off-site treatment and disposal methods dominate the management of produced water with higher TDS that can occur later in operations. Here we focus on the wastewater management options associated with produced waters that generally occur off-site in particular disposal through wastewater treatment and beneficial use from road spreading for de-icing. The level of treatment required varies for each of the wastewater management options (NRDC, 2012).

Direct discharges from unconventional oil and gas extraction are subject to NPDES permit regulations. Indirect discharges to Publicly Owned Treatment Works (POTWs) are subject to the General Pretreatment Regulations (http://water.epa.gov/scitech/wastetech/guide/oilandgas/unconv.cfm). Consequently, disposal of untreated water typically occurs through by pumping the fluid into Class II underground injection control (UIC) wells. This option creates a risk of earthquakes (Keranen et al., 2013) and can require transportation of wastewater over long distances. In Pennsylvania, there are a limited number of permitted injection wells, hence wastewater is often transported to Ohio and West Virginia. Wastewater from the Marcellus has also been sent to publicly owned treatment works (POTWs) in Pennsylvania. However, POTWs do not have the capability to remove most dissolved solids and therefore most salts that enter these treatment facilities will be indirectly discharged into receiving waters. In 2010, the Pennsylvania Department of Environmental Protection (PA DEP) issued regulations that prohibited the release of effluent to surface water of TDS in excess of 500 mg/L (25 Pennsylvania Code Chapter 95), but more than 27 POTWs were grandfathered into less stringent regulations if they did not increase their total output and continued to meet their existing discharge permit criteria (PA DEP, 2011a). As of May 19, 2011 all POTWs, including those previously grandfathered, were asked to voluntarily stop accepting shale gas wastewater (PA DEP, 2011a). An alternative to POTW treatment for removal of suspended solids and organic constituents is treatment at dedicated brine or industrial wastewater facilities, also called centralized waste treatment (CWT) facilities. These plants use many of the same treatment processes that are found in POTWs but may also add coagulation and precipitation techniques to remove dissolved solids (Ferrar et al., 2013). Additionally, POTWs typically have some form of biological treatment such as aeration basins or trickling filters.

In many states untreated produced water is used for dust control on unpaved roads and for deicing roads during the winter (Eckstein, 2011; Gilday et al., 1999). Although produced waters from the Marcellus are prohibited from this beneficial use option, brines from conventional oil and gas operations are permitted for beneficial use such as road spreading if they meet certain water quality criteria (PADEP, 2011b).

There has been a rapid change in disposal practices in Pennsylvania since 2008. Based on data from PA DEP from 2008, almost half of the produced water from both conventional and unconventional gas extraction (~45%) went to municipal POTWs, approximately 28% of the produced water went to CWT facilities, and about 14% was reused in the hydraulic fracturing process (reuse). More than 3% was used in road spreading and approximately 4% was transported to wells (UIC) for disposal (Table 1). It should be noted that prior to 2010, data on wastewater from gas extraction was not separated by well type. Although the 2012 data is separated into conventional and unconventional, it is evident that changes in policies regarding disposal of flowback and produced waters through POTWs had produced a dramatic shift in the disposal methods for produced waters (Table 1). Given limited wastewater management options within the region, reuse in other hydraulic fracturing operations has become the most common water management practice. Use of POTWs for handling wastewater has been almost completely eliminated. The treatment of waste by CWTs has also been reduced, while transporting waste to injection well sites has increased.

Table 1
Disposal methods used in Pennsylvania and the percent of total for 2008 disposal and 2012 disposal. Marcellus waste was differentiated from non-Marcellus waste in 2012.

Disposal method	2008 (Both)	2012 Non-Marcellus	2012 Marcellus
CWT	26.7%	18.0%	16.3%
Injection	3.9%	17.3%	12.4%
Landfill	0.0%	0%	0.4%
POTW	44.7%	0.9%	0%
Other	4.2%	0%	0%
Reuse	14.2%	61.6%	69.8%
Road spreading	3.3%	1.0%	0%
Storage	0.01%	1.1%	1.1%
Treatment	3.0%	0%	0%

In light of the disposal practices highlighted above, we hypothesized that constituents in produced waters that have an affinity for sediment particles could be accumulating in specific surficial environments. This study focused on near-surface sediments below POTW and CWT outfalls for facilities that did and in some cases continue to process oil and gas brines as well as soils on the margins of roads in regions known to accept and utilize petroleum-related brine for de-icing and dust control, focusing on Ba, Ca, Na, Ra, and Sr.

We designed the study to focus on Ra because as a radioactive element, it has the potential to pose a risk to human and ecosystem health, and is known to be highly elevated in many produced water samples from the basin (Rowan et al., 2011). In surface and shallow subsurface environments, Ra can be relatively soluble and, therefore, mobile in groundwater over a range of pH and Eh (redox) conditions. Radium also may be adsorbed onto clay particles or onto oxide grain coatings. The half-lives of the two principal isotopes, Ra-226 and Ra-228, are 1600 and 5.75 years, respectively. Several half-lives are required for these isotopes to decay to negligible levels. Therefore, we hypothesized that they persist in the surface environment and may be accumulating in areas of oil or gas development.

Ba, Ca, Na, and Sr are all chemically similar to Ra and known to elevate in produced waters and therefore we extended our analyses to include these elements. Ba belongs to the alkaline-earth group and geochemically resembles Ca and Sr. It may also resemble Ra in the environment, can accumulate in Mn oxides in soil, and has also been associated with drilling-related discharges (Philips and Rainbow, 1993). Barite is soluble enough to be taken up by plants growing on Ba-rich soils and can accumulate to levels which could be potentially toxic to animals (Norrish, 1975).

Elements in sediments and soils are present in various forms. For example, they may be adsorbed (clays, iron oxyhydroxides), complexed with organic matter, reside in the lattice of residual primary minerals (silicates) or secondary minerals (sulfates, oxides). The relative mobility of each element depends upon its form and the physico-chemical environment. Mobile elements could be solubilized due to changes in the environment whereas residual (or non-mobile) elements are associated with stable fractions of the soil or sediment and would not easily become mobile (Leleyter et al., 2012). The objective of this study was to assess the accumulation in sediments and soils of dissolved alkali-earth elements from produced waters. These elements would accumulate in the mobile phases of the sediment and soils and would not likely partition into residual primary mineral phases. Thus, our study design was focused on quantifying the element concentrations in the potentially