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Identification and quantification of regional brine and road salt sources in watersheds along the New York/Pennsylvania border, USA

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ABSTRACT

The ecologically sensitive Susquehanna River Basin (SRB) is an important recharge area and drinking water source for a large population in the northeastern United States. Seasonal road salt application, the presence of regional brines at shallow depths, and produced waters associated with active and legacy conventional Upper Devonian oil and gas wells could increase total dissolved solids (TDS) in groundwater and streams. This study focused on SRB watersheds along the New York/Pennsylvania border, in order to assess current water quality and to establish baseline geochemistry for ground and surface water in a region with potential for increased development of the Marcellus Shale and other unconventional shale gas units. Geochemical composition was determined for 300 stream samples collected from ten sites in four watersheds over variable seasonal flow conditions, and for groundwater from over 500 drinking water wells in this region. Results indicate that many streams and groundwater wells in the study area have elevated TDS levels that indicate pre-existing contributions from saline sources. Dilution of these inputs with fresh water, and the lack of low-level trace element concentrations and isotopic composition in many water quality analyses, highlight the need for alternate robust and sensitive chemical signatures. Comparison with Cl/Br anion ratios and $^{87}Sr/^{86}Sr$ isotope ratios indicate that the (Ba + Sr)/Mg ratio can be used to discriminate between road salt and regional brine in these cases, and mixing models show that even small additions (0.1–0.01%) of these contaminants can be detected with this cation ratio. The (Ba + Sr)/Mg ratio may be even more sensitive (by an order of magnitude) to incursions of Marcellus Shale produced water, depending on the composition of Marcellus produced waters in this region. This study highlights the need for baseline sampling of freshwater reservoirs and the characterization of potential high TDS sources at a local and regional scale.

1. Introduction

The expansion of unconventional shale gas development in areas underlain by the Marcellus and Utica shales in the Appalachian region of the northeastern United States has raised concerns about the protection of sensitive surface and groundwater resources (Soeder and Kappel, 2009; Wilson and VanBriesen, 2012; States et al., 2013; Vidic et al., 2013; Soeder et al., 2014; Vengosh et al., 2014). Over a million homeowners in Pennsylvania and about a third of New York State's population rely on groundwater for drinking water (NYDEC, 2014; PADEP, 2014). The Susquehanna River Basin (SRB) watershed is of particular importance in the northeastern USA because the river and its tributaries drain 71,000 km^2 that encompass the eastern half of Pennsylvania and provide over 50% of the water entering the Chesapeake Bay (PADEP, 2014; SRBC, 2014). It is critical to collect water quality data from sensitive ground and surface waters, both to establish baseline values, and in some cases to characterize and identify the presence of pre-existing constituents that could affect accurate interpretation of shifts in water quality subsequent to natural gas development.

Risks to surface and groundwater quality related to shale gas development include accidental spills or improper disposal of drilling fluids or produced water, wastewater discharge, and migration into or displacement of shallower groundwater through fractures (Gregory et al., 2011; National Research Council, 2014; Soeder et al., 2014; Vengosh et al., 2014). However, in the SRB watersheds, the presence of pre-existing sources of high TDS fluids such as naturally occurring brines in the subsurface or discharging from springs, produced water from legacy or active conventional oil and gas wells, and the widespread application of road salt present a challenge to the interpretation of "change in water quality due to drilling operations" if appropriate baseline data are not collected.

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Water quality in the headwater watersheds of the SRB in the Northern Tier of Pennsylvania and Southern Tier of New York is tracked on a real-time basis by the Susquehanna River Basin Commission (SRBC) using a network of over 60 water quality sondes (SRBC, 2013a) as well as by other organizations (Bradford County Conservation District in northeastern Pennsylvania, J. Quatrini personal communication 2012; Wilkes University, 2013). Stream monitoring and baseline water quality programs in many SRB headwater watersheds in New York presently include measurement of field parameters such as specific conductance, temperature, and pH (New York Water Sentinels, 2013; Sierra Club Susquehanna Group, S. Lauffer personal communication 2013), as well as grab sampling followed by analysis for major inorganic constituents (Catskill Headwaters, 2013; Otsego County, 2013; SRBC, 2013b). Publicly accessible databases also aid in dissemination of water quality data (Community Science Institute, 2013; Shale Network, 2013) as well as to educate the public about collection and interpretation of water quality data (Dickinson College, 2013).

In this study, we present field and geochemical data for surface and groundwaters from the Southern Tier of New York State (Broome and Tioga Counties) and the Northern Tier of Pennsylvania (Bradford and Susquehanna Counties) within the headwater region of the SRB. Over 500 groundwater samples were obtained from local homeowner water wells, and surface water was collected over three seasons from ten stream sites in four adjacent watersheds, including several directly impacted by discharges from a natural brine spring at Salt Springs State Park. Geochemical data from the Salt Springs brine, road salt, and produced water from Marcellus shale gas wells were compared in order to identify geochemical signatures and allow discrimination among sources.

This study aids in the characterization of surface and groundwater in the ecologically and economically sensitive SRB headwaters by (1) expansion of the database of field and analytical baseline data for surface waters from four adjacent watersheds and over 500 residential drinking water wells; (2) determination of discharge-dependent geochemical variations that can identify the source of high TDS in impacted surface and groundwater; and (3) development and testing of geochemical fingerprints that can be used to identify and quantify high-chloride inputs in cases where baseline data are lacking or dilution or overlap of signatures renders traditional anion–cation ratios or Sr isotopic composition ineffective. The water quality analysis and metrics presented can serve as high TDS source tracers to assist stakeholders in short and long term water quality assessments.

2. Sources and signatures of high TDS inputs to the Upper Susquehanna watershed

2.1. Previous work on geochemical signatures

Chloride concentrations combined with Cl/Br ratios have been used to discriminate between road salt sources and natural brine and/or produced water from oil and gas wells (Rittenhouse, 1967; Richter and Kreitler, 1991; Whittemore, 1995; Uliana, 2005; Mullaney et al., 2009; Wilson and VanBriesen, 2012; Ferrar et al., 2013; Llewellyn, 2014). In the glacial aquifer system of the northern United States, Mullaney et al. (2009) used Cl/Br ratios to identify mixing of groundwater with chloride sources including road salt, subsurface brines, sewage and animal waste, fertilizer and seawater. Although Cl/Br ratios have been used extensively to fingerprint road salt and oil and gas well brines, when diluted in stream or groundwater, low Br detection limits ($\leqslant$0.01 mg/L) are required. Therefore, most pre-drilling datasets from the region do not include Br, or it is reported as below detection (Taylor, 1984; Williams et al., 1998; Llewellyn, 2014). In addition, Sr isotopes have been used to differentiate between flowback and produced water from Marcellus shale gas wells, Upper Devonian conventional gas wells, acid mine drainage, and surficial background values (Chapman et al., 2012, 2013; Kolesar Kohl et al., 2014). However, many archival records do not include isotopic analyses. Therefore, other sensitive geochemical signatures that can distinguish between potential contaminant sources are needed in order to use pre-drilling archival datasets as records of baseline water quality.

2.2. Potential high TDS sources in the SRB watershed

2.2.1. Road salt

Chloride loading in watersheds due to road salt de-icing has been documented across northeastern North America for the past 50 years, in many cases corresponding to road density (Williams et al., 1999; Rhodes et al., 2001; Kaushal et al., 2005; Kelley et al., 2008; Shaw et al., 2012). Road salt used in the study area is composed primarily of halite (NaCl), containing minor Mg, Ca, Sr and Ba (Titler, 2011), and is generally sourced from Silurian-aged units to the north of the study area; salt used on local upstate roadways in New York watersheds is mined in Lansing, New York (Cargill, 2014). Scouring of Silurian salt from outcrops during the last glaciation has resulted in localized halite brine sources in glacial drift deposits in upstate New York (Yager et al., 2007). However, the predominant source of halite signatures in surface and groundwater from this study are more likely due to the widespread use of road salt throughout the study area. Mullaney et al. (2009) reported that Cl/Br ratios for road salt (halite) were between 3000 and 10,000.

2.2.2. Regional subsurface brines

Natural gas has been produced in the study area for over a century, and numerous active and abandoned wells date back to 1895 in New York and Pennsylvania (Carter and Harper, 2002; Dresel and Rose, 2010; Osborn and McIntosh, 2010; Williams, 2010). Williams (2010) reported that water quality in the region is strongly dependent on geomorphology. His evaluation of well logs found that the transition from freshwater to saline occurs below ~245 m depth in upland areas, and only ~60 m in valleys; groundwater in Upper Devonian units such as the Bradford Sands, which contain conventionally developed gas fields, is generally salty. Seeps of hydrocarbons and some artesian flow of subsurface brines are also documented, with migration occurring primarily along NNE-SSW structural trends along the Alleghenian orogenic front (Carter and Harper, 2002; Williams, 2010; Llewellyn, 2014). These regional (natural) brines typically occur in valley floor settings closer to the freshwater-saline transition and are commonly associated with faults or inferred structures (Llewellyn, 2014). One such brine is discharged at the surface in Salt Springs State Park, Susquehanna County, Pennsylvania; Warner et al. (2012) report a Cl/Br value of 106 (n = 1) from Salt Spring.

2.2.3. Produced water from Marcellus Shale gas wells

While there is currently no activity in the New York portion of the study area, Marcellus Shale gas exploration could begin within the next few years. The volume of water that flows out of hydraulically fractured Marcellus Shale gas wells decreases significantly as production continues, but total dissolved solid (TDS) content, including concentrations of Sr, Ba and Ra, increase significantly over time (Blauch et al., 2009; Hayes, 2009; Chapman et al., 2012; Capo et al., 2014). Late-stage (>14 days after fracturing) produced waters from Marcellus Shale gas wells are sodium–calcium–chloride (Na–Ca–Cl) brines with TDS contents that can exceed 300,000 mg/L (Barbot et al., 2013; Haluszczak et al., 2013).