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Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale

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ABSTRACT

Organic substances in produced and formation water from coalbed methane (CBM) and gas shale plays from across the USA were examined in this study. Disposal of produced waters from gas extraction in coal and shale is an important environmental issue because of the large volumes of water involved and the variable quality of this water. Organic substances in produced water may be environmentally relevant as pollutants, but have been little studied. Results from five CBM plays and two gas shale plays (including the Marcellus Shale) show a myriad of organic chemicals present in the produced and formation water. Organic compound classes present in produced and formation water in CBM plays include: polycyclic aromatic hydrocarbons (PAHs), heterocyclic compounds, alkyl phenols, aromatic amines, alkyl aromatics (alkyl benzenes, alkyl biphenyls), long-chain fatty acids, and aliphatic hydrocarbons. Concentrations of individual compounds range from <1 to 100 μg/L, but total PAHs (the dominant compound class for most CBM samples) range from 50 to 100 μg/L. Total dissolved organic carbon (TOC) in CBM produced water is generally in the 1–4 mg/L range. Excursions from this general pattern in produced waters from individual wells arise from contaminants introduced by production activities (oils, grease, adhesives, etc.). Organic substances in produced and formation water from gas shale unimpacted by production chemicals have a similar range of compound classes as CBM produced water, and TOC levels of about 8 mg/L. However, produced water from the Marcellus Shale using hydraulic fracturing has TOC levels as high as 5500 mg/L and a range of added organic chemicals including, solvents, biocides, scale inhibitors, and other organic chemicals at levels of 1000 s of μg/L for individual compounds. Levels of these hydraulic fracturing chemicals and TOC decrease rapidly over the first 20 days of water recovery and some level of residual organic contaminants remain up to 250 days after hydraulic fracturing. Although the environmental impacts of the organics in produced water are not well defined, results suggest that care should be exercised in the disposal and release of produced waters containing these organic substances into the environment because of the potential toxicity of many of these substances.

1. Introduction

Produced water is any water produced from a hydrocarbon (gas, liquid) well, including flowback water, formation brine, water condensing from the gas phase, and mixtures thereof (also referred to as co-produced water). Large volumes of produced water may result from wells drilled into overpressured formations containing oil and natural gas (Clark and Veil, 2009). In coalbeds containing natural gas (coalbed methane or CBM), the water needs to be removed to reduce the hydrostatic pressure and allow the gas to release from the coal for collection (Veil et al., 2004). Produced water usually contains large volumes of naturally occurring water (formation water), often of brackish to brine salinity, which is present in oil and gas reservoirs, and associated with the formation from which the oil and gas are extracted. In many cases, however, additional water is injected into wells to either enhance the recovery of oil (Satter et al., 2008), or for hydraulic fracturing operations to release gas from coal or shale (EPA, 2010). Hydraulic fracturing is used extensively in both CBM and shale gas production. The injected water contributes to the produced water of oil and gas operations. Injected water can originate from different sources, including: surface water, groundwater, and water produced from previous oil and gas extraction and stored for repeated use (Gregory et al., 2011). Much of the injected water is returned to the surface within the first few days and referred to as flowback water (GWPC and ALL Consulting, 2009). Flowback water consists primarily of the water injected into the ground and admixed formation water, and is often stored in ponds or tanks for

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reuse (Rassenfoss, 2011). Injected water may alter the chemical composition of the original formation water, and thus of produced water.

The responsible disposal of produced water is a major issue for oil and gas operations because of the large volumes of water, the chemical composition of produced water, and limitations on disposal options (ALL Consulting, 2003; Clark and Veil, 2009). The chemical composition of produced water is variable, and determined by the chemical composition of the local formation water, and by chemicals added from natural gas production. Production chemicals include those used for hydraulic fracturing, and other purposes (e.g. corrosion inhibitors, antifreeze, biocides, plastics, and adhesives). Produced water from CBM production can range from low total dissolved solids (TDS), circumneutral pH, fresh water composition characteristic of most produced water from the Powder River Basin (Advanced Resources International Inc., 2003; Rice et al., 2000), to much higher TDS CBM plays in the Uinta (UT) and parts of the Black Warrior (AL) Basins (O'Neil et al., 1993; Rice, 2003; Rice and Nuccio, 2000; Van Voast, 2003). Produced water from natural gas extraction in many shale plays is hypersaline. For example, produced water from natural gas production in the Marcellus Shale (USA) has typical TDS values of about 200,000 mg/L (Hayes, 2009; Silva et al., 2012). TDS values of flowback water collected during the first 10–20 days of well operation are sometimes much lower due to dilution of the formation water by fresher hydraulic fracturing fluids, unless saline water is also used for hydraulic fracturing (Silva et al., 2012). In addition to salts, produced water may also contain a host of other dissolved inorganic substances, including metals (e.g. As, B, Ba, Cd, Co, Cr, Fe, Hg, Ni, V, Zn) and radioactive substances such as $^{238,\ 235}$U, ^{232}Th, $^{226,\ 228}$Ra, ^{222}Rn, and ^{40}K (Barbot et al. 2013; Chapman et al., 2012; Kargbo et al., 2010; Rowan, 2011; Rowan et al., 2011). Some of these substances originate from the formation water, some from the solid substrate phase (formation rock) and mobilized during extraction operations (e.g. metals such as Ba, and As, and naturally occurring radioactive materials or NORM), and some are added to facilitate production, such as B salts as crosslinker and viscosity enhancer, and radioactive tracers to determine the injection profile and location of fractures produced by hydraulic fracturing (e.g. ^{41}Ar, ^{133}Xe, ^{131}I); (API, 2010; Chapman et al., 2012; Steuber and Walter, 1991).

Organic substances are also present in produced water from oil and gas extraction. Like inorganic constituents, organic substances in produced water can originate from the formation water, the solid phase associated with the formation water (coal or shale), oil present in the formation, and from organic chemicals added during production. Although hydraulic fracturing fluids used in CBM and shale gas production are composed mainly of water and sand (98–99.5%), the additional additives include a host of organic chemicals to facilitate gas release (Arthur et al., 2009). The organics used in hydraulic fracturing in CBM and shale gas production are similar and include: biocides (e.g. brominated nitrilopropionamides), cross linkers (e.g. ethylene glycol), delivery gels (e.g. guar gum and diesel fuel), foaming agents (e.g. ethanol), corrosion inhibitors (e.g. methanol), and many other compounds (EPA, 2004; Waxman et al., 2011). While a large literature exists on organic substances present in produced water and oil field brines from petroleum production (Carey et al., 1992; Grahl-Nilsen, 1987; Higashi and Jones, 1997; Utvik, 1999; Willey et al., 1975), few studies have been published on organic substances present in produced water from CBM and shale gas extraction (Dahm et al., 2011, 2013; Hayes, 2009; Huang, 2008; Orem et al., 2007; Veil et al., 2004). Here, we compare and contrast organic substances in produced water from CBM and shale gas from different areas, primarily within the USA. An understanding of the composition of organic matter in produced water is important since these compounds represent contaminants that may impact the environment if released into watersheds or possibly impact human health if released into drinking water supplies (Colborn et al., 2011; Kargbo et al., 2010; Orem et al., 2007). Organic substances in produced water can also present a problem in membrane methods used to reduce the TDS of produced water through fouling of the membranes and reducing efficiency of this approach (Gregory et al., 2011). Finally, these organic substances, especially compounds in the formation water, may act as substrate driving microbial methanogenesis in both coalbeds and shale (Jones et al., 2010). Understanding the types of organic compounds present in formation water that drive microbial methane production may be useful in predicting where microbial gas is accumulating, and provide insight on the biodegradation pathway leading to microbial methane production (Orem et al., 2010).

2. Study areas and sampling

Produced and formation water samples for this study were collected from CBM and shale gas locations across the USA (Fig. 1), including: the Marcellus Shale (Pennsylvania), the New Albany Shale (Indiana and Kentucky), Illinois Basin CBM (Illinois), Black Warrior Basin CBM (Alabama), Powder River Basin CBM (Wyoming), Tongue River Basin (the northern part of the Powder River Basin, Montana), and Williston Basin CBM (North Dakota). All samples collected were analyzed.

Water samples were collected directly from active well heads. Sample containers were filled to the top so that minimal to no headspace was present. Subsamples for total dissolved organic carbon (TOC) and volatile fatty acids (VFAs) were filtered using a clean glass syringe and Whatman Polyethersulfone (PES) 0.2 μm syringe filters into clean amber glass vials and plastic scintillation vials, respectively. VFA samples were frozen on dry ice to prevent biodegradation, and TOC samples were kept cool on water ice in the field and later refrigerated in the lab until analysis within one week. Subsamples for analysis of extractable hydrocarbons were filtered using Whatman GF/F 0.7 μm filters into 1 L amber glass bottles with Teflon lined screw caps, and approx. 60 mL dichloromethane (DCM) was added to the filtrate in the field to prohibit biodegradation, and the samples were stored in coolers in the dark. Amber bottles were used to limit photodegradation of TOC and extractable hydrocarbons. All filtrations were done using an all glass Millipore filtration apparatus and a vacuum or hand pump. Glassware and glass bottles were precleaned for organic contaminants either by baking in a furnace (450 °C for 2 h) or by washing with DCM (Orem et al., 2007).

Field blanks, consisting of MilliQ water taken into the field in clean glass bottles and processed in the same manner as produced water samples, were used to assess any contamination from sample handling or processing. Field blanks consistently showed little or no contamination: TOC values reflected that of pure Milli-Q water, VFAs were not detected, and extractable hydrocarbons consisted of little other than small peaks for phthalates (from plastic coated on exterior of sample bottles to protect from breakage during shipping; Orem et al., 2007).

3. Analytical methods

TOC was determined using a Shimadzu TOC-VCPH analyzer equipped with a catalytically-aided 680 °C combustion chamber and normal sensitivity catalyst. Standardization was based on a 6-point calibration curve using a potassium phthalate standard (100 mg/L, or 10 mg/L depending on the TOC range of the samples). The detection limit is 0.1 mg/L (100 ppb). Milli-Q water was used as a blank, and each sample was injected at least two times to ensure data consistency.

Filtered produced water samples were analyzed for VFAs using high performance liquid chromatography (HPLC) with a Waters Corporation Alliance HT autosampler and 996 photodiode array detector, and an Alltech Prevail organic acid column (150 mm × 4.6 mm; 5 μm packing). A solution of KH_2PO_4 (25 mmol/L, pH 2.5) was used as eluent, with a flow rate of 1.5 mL/min. Chromatograms were extracted from the diode array spectrum at 205 nm. Standard solutions were prepared from serial dilutions of 2000 mg/L stock standards of pure fatty acids (C_1–C_4) in Milli-Q water. The detection limit ranged from 0.1 to 1.0 mg/L (1.7–17 μmol/L), depending on the complexity of the produced water fluid matrix.