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Characterization of hydraulic fracturing flowback water in Colorado: Implications for water treatment

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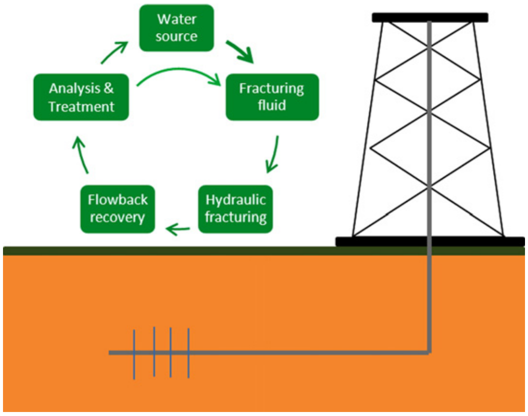
HIGHLIGHTS

- Flowback from the DJ basin (CO) was analyzed using a suite of analytical tools.
- The flowback contained salts, metals and high levels of dissolved organic matter.
- Organic matter was comprised of fracturing fluid additives and degradation products.
- Water analysis and treatability tests served to indicate suitable treatments.
- Example: aeration/precipitation/disinfection deemed suitable for flowback recycling

GRAPHICAL ABSTRACT



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ABSTRACT

A suite of analytical tools was applied to thoroughly analyze the chemical composition of an oil/gas well flowback water from the Denver–Julesburg (DJ) basin in Colorado, and the water quality data was translated to propose effective treatment solutions tailored to specific reuse goals. Analysis included bulk quality parameters, trace organic and inorganic constituents, and organic matter characterization. The flowback sample contained salts (TDS = 22,500 mg/L), metals (e.g., iron at 81.4 mg/L) and high concentration of dissolved organic matter (DOC = 590 mgC/L). The organic matter comprised fracturing fluid additives such as surfactants (e.g., linear alkyl ethoxylates) and high levels of acetic acid (an additives' degradation product), indicating the anthropogenic impact on this wastewater. Based on the water quality results and preliminary treatability tests, the removal of suspended solids and iron by aeration/precipitation (and/or filtration) followed by disinfection was identified as appropriate for flowback recycling in future fracturing operations. In addition to these treatments, a biological treatment (to remove dissolved organic matter) followed by reverse osmosis desalination was determined to be necessary to attain water quality standards appropriate for other water reuse options (e.g., crop irrigation). The study provides a framework for evaluating site-specific hydraulic fracturing wastewaters, proposing a suite of analytical methods for characterization, and a process for guiding the choice of a tailored treatment approach.

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1. Introduction

Increased use of hydraulic fracturing for unconventional gas exploration has resulted in substantial interest in the environmental impacts of this technology. One of the major concerns is the generation of large volumes of flowback water, and its potential adverse effects on the environment and on human health (Vengosh et al., 2014). During hydraulic fracturing, up to 4 million gal of water-based fluid is injected into a single drilled well, to initiate and expand fractures, as well as for proppant transport (i.e., sand or ceramic materials); of which 10–70% is subsequently recovered as flowback (API, 2010). This impaired water stream contains high concentrations of potentially hazardous organic and inorganic constituents and requires some degree of treatment before the water is reused or discharged into the environment.

Until recent years, the most popular "treatment" for flowback was the disposal of the water into deep injection wells. However, this technique is becoming less viable due to limited access to disposal wells in many drilling locations, and increased pressure from regulatory authorities and the public for a more sustainable solution (Gregory et al., 2011; Lutz et al., 2013). These pressures, along with stresses on local water resources and potential cost savings, have led the industry to search for alternative treatment solutions, many of which would enable beneficial water reuse (Mauter et al., 2014).

The choice of suitable treatment approaches depends largely on the composition of the flowback water, which is typically a mixture of the original injected additives as well as substances from the subsurface formation that accumulate in the water down-hole. The original additives, injected to facilitate the fracturing process and prevent problems during well operation mainly include gelling agents, friction reducing polymers, corrosion and scale inhibitors, and biocides (FracFocus, 2014). Some of these chemicals are recovered unchanged, while others either react under the conditions of the fracturing process or are microbially altered to form degradation and reaction products (Orem et al., 2014). Olsson et al. (2013), for instance, found high concentrations of acetate and formate in flowback water from two different fracturing sites in Germany (up to 480 and 190 mg/L, respectively), whereas these substances were present at extremely low concentrations in formation water from a well unimpacted by hydraulic fracturing. The researchers concluded that acetate and formate were likely the degradation products of polymers used in the fracturing fluid.

Substances in flowback water coming from the subsurface may include salts, metals and soluble organic compounds, depending on the location and nature of the geological formation. Acharya et al. (2011) showed large variations in the concentration of total dissolved solids (TDS) in flowback water from different shales, with average values ranging from 13,000 mg/L (Fayetteville shale) to 120,000 mg/L (Marcellus shale). Boschee (2014) reported TDS levels in the range of 20,000–65,000 mg/L for flowback and produced water from the Denver–Julesburg (DJ) basin, and 150,000–300,000 mg/L for water from the Bakken formation.

Clearly, understanding the composition of the flowback water is essential for assessing its reuse potential and for implementing a suitable treatment process to improve water sustainability. The goals of this research were to (i) demonstrate the use of a suite of analytical tools for an in depth analysis of hydraulic fracturing flowback, using the DJ basin (CO) as an example, and, (ii) use the analytical data to propose suitable strategies for the treatment of the flowback water for beneficial reuse. In addition, the paper provides information on the composition of flowback water in the DJ basin, which is presently highly underexplored (relative to other basins).

2. Material and methods

The flowback water was a composite sample taken by the well operator and delivered under a non-disclosure agreement, mainly with regard to sampling period, specific well location, and composition of the original fracturing fluid. The sample was filtered upon receipt with a 0.45 μm cellulose acetate filter (prewashed with 1 L deionized water and 200 mL flowback) and analyzed for general quality characteristics, inorganic constituents, and trace organic compounds. The selection of examined parameters was based on a list of potential flowback constituents, established by Hayes (2009) following comments received from regulatory agencies and members of the oil and gas industry.

2.1. General quality parameters

Dissolved organic carbon (DOC) was measured after dilution using a TOC-V_{SCH} analyzer (Shimadzu Corp., Japan). Chemical oxygen demand (COD) was measured using HACH (Loveland, CO) COD kits and a DR5000 spectrophotometer (after water dilution). Biochemical oxygen demand (BOD_5) was analyzed according to standard method SM5210B. Volatile Fatty Acids (e.g., acetic acid) and inorganic anions (e.g., Cl^-, Br^-) were measured using ion chromatography (IC Dionex 4500I). Total recoverable phenolics were measured in accordance with EPA method 420.4. Other general quality parameters were analyzed using either EPA or standard methods (see Table 1). Analyses were conducted at least in duplicates in most cases, with relative standard deviations typically below 10%. Naturally occurring radioactive materials (NORM), occasionally detected in flowback, were not analyzed in the present study, because they are not considered flowback contaminants of concern in Colorado (STRONGER, 2011).

2.2. Elemental analysis

Selected elements were analyzed at the Laboratory for Environmental and Geological Studies — LEGS (Department of Geological Sciences, University of Colorado at Boulder, CO), using a Perkin Elmer SCIEX inductively coupled plasma mass spectrometer (ICP-MS, Elan DRC-e). Samples were first diluted by ×10, ×100 and ×1000, and the average value is reported (for results above the analytical method detection limit [MDL]). Concentrations of the major ions (e.g., Ca^{2+}, Mg^{2+}, Na^+) were validated by inductively coupled plasma optical emission spectroscopy (ICP-OES, ARL 3410+, Thermo Scientific).

Table 1
General quality parameters, inorganic ions and select organic compound concentrations for the flowback sample.

Parameter	Analytical method	Units	Value
Bulk parameters			
pH			6.8
DOC	SM 5310B	mgC/L	590
Alkalinity	HACH 8203	mg $CaCO_3$/L	150
TDS	SM 2540C	mg/L	22,500
COD	EPA 5220D		1218
BOD_5	SM 5210B		1100
Oil & grease	EPA 1664A		59
TSS	SM 2540D		360
Inorganic ions			
Ammonia as N	EPA 320.1	mg/L	24.7
NO_3 as N	IC		5.2
Chloride (Cl^-)	IC		13,600
Cyanide, total	EPA 335.4		0.055
Bromide (Br^-)	IC		87.2
Sulfide (S^{2-})	SM 4500 S2 D		0.31
Sulfate (SO_4^{2-})	IC		1.3
Others			
Total recoverable phenolics	EPA 420.4	mg/L	1.4
Acetic acid	VFA-IC		1600
n-Butyric acid	VFA-IC		19
Propionic acid	VFA-IC		33