

Identifying Well Contamination through the use of 3-D Fluorescence Spectroscopy to Classify Coalbed Methane Produced Water

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S Supporting Information

ABSTRACT: Production of unconventional gas resources commonly requires the use of hydraulic fracturing and chemical production well additives. Concern exists for the use of chemical compounds in gas wells due to the risk of groundwater contamination. This study focuses on a proposed method of identifying groundwater contamination from gas production. The method focuses on the classification of naturally occurring organic signatures of coalbed methane (CBM) produced water compared to anthropogenic organic compounds. The 3-D fluorescence excitation–emission matrix (EEM) spectra of coalbed methane produced water samples revealed four peaks characteristic of coalbed methane produced water: Peak P (aromatic proteins region), Peak M₁ (microbial byproducts region), Peak M₂ (microbial byproducts region), and Peak H (humic acid-like region). Peak H is characteristic of the coal–water equilibria present in all basins, while peaks P and M₂ correlate with microbial activity in basins with biogenic methane generation pathways. Anthropogenic well additives produce EEM signatures with notable flooding of peaks P, M₁, M₂, and H, relatively higher overall fluorescence intensity, and slightly higher DOC concentrations. Fluorescence spectroscopy has the potential to be used in conjunction with groundwater contamination studies to determine if detected organic compounds originate from naturally occurring sources or well production additives.



INTRODUCTION

Coalbed methane (CBM) is an unconventional natural gas resource. Low carbon emitting energy sources, such as natural gas from organic-rich coals and shales, are becoming increasingly important because of climate change and rising energy needs worldwide.¹ Unconventional gas resources commonly require the use of hydraulic fracturing and/or chemical well production additives to economically generate energy resources. Concern exists for the use of chemical compounds, such as biocides and antiscalants, in gas production due to the risk of groundwater contamination. Production and fracturing additives are commonly complex organic compounds, which are difficult to identify in waters that naturally contain complex organics such as those in producing formations. In 2003, the U.S. EPA completed a study outlining the dangers of hydraulic fracturing associated with CBM production on drinking water supplies.² This EPA study investigated basin geology, hydrologic connectivity, produced water quality, and the potential contamination of drinking water by hydraulic fracturing. The need exists to develop criteria and methods for differentiating groundwater naturally impacted by oil and gas formation hydrocarbons and

groundwater supplies impacted by anthropogenic chemicals used for fracturing and well production.

Produced water is defined as formation water that is brought to the surface during gas production. In CBM gas wells, water production is necessary to facilitate the lowering of hydrostatic pressure in the coal seam allowing gas desorption and production. Formation water, present at the time of coal deposition, carries water quality characteristics of the depositional environment, ranging from continental or fresh water to brackish or marine.³ Plant organic matter deposited in these environments is broken down both physically and chemically by biotic and abiotic processes to form peat, after which heat and pressure slowly transform the peat into coal through the process of maturation.⁴ CBM coal seams can act as regional aquifers and are further influenced by groundwater recharge and nutrient transport and cycling. Aquifer interactions include precipitation/dissolution reactions, cation

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exchange, and oxidation–reduction reactions.⁵ Finally, anthropogenic activities, such as drilling, hydraulic fracturing, and pumping, have the potential to influence the organic matter signature of produced water.

Coalbed methane produced water is likely to have unique natural organic matter signatures due to contact with the coal formation and potential microbial activity related to secondary biogenic methane production. Van Voast⁶ describes waters associated with CBM as having a common chemical character that can be used as an exploration tool, regardless of formation lithology or age. While inorganic constituents in CBM produced water have been well described,^{6–10} the presence and character of natural organic matter (NOM) in CBM produced water has not been widely studied. NOM in CBM produced water may lend insight into baseline signature of basins that have undergone coal maturation and/or methane generation.

Classification of the naturally occurring organic signature in comparison to anthropogenic organic compounds requires a method capable of differentiating contamination in groundwater resources due to oil and gas production chemicals. Fluorescence spectroscopy is a fingerprinting tool used to characterize NOM present in natural waters. This characterization technique scans excitation and emission wavelengths simultaneously to generate 3-D excitation–emission matrix (EEM) spectra of water samples.¹¹ EEM spectra can be used to differentiate certain organic carbon source materials and environmental pollutants.¹² EEM spectra from CBM produced water are hypothesized to express a baseline signal originating from interactions of the formation water with the coal and/or byproducts of the methane generation process. Spectra generated from the presence of anthropogenic compounds are expected to be easily distinguished from the naturally occurring baseline spectra.

The objectives of this study were therefore to (1) establish characteristic EEM fingerprints of CBM produced water, (2) identify sources of NOM in the system through comparisons to EEM spectra generated from various potential organic matter sources, and (3) identify and distinguish indicators of anthropogenic contamination due to well production additives from naturally occurring organic signatures.

MATERIALS AND METHODS

Water samples were collected at CBM wellheads from four major CBM production basins in the Rocky Mountain region during six sampling campaigns that occurred from April 2009 to August 2010. Twenty samples were obtained from wells in the Atlantic Rim portion of the Greater Green River Basin, 31 samples from the Powder River Basin, 40 samples during three sampling campaigns to the Raton Basin, and 20 samples from the San Juan Basin. Further information on these basins and sampling locations is provided in Supporting Information (SI) Table 1. Collected samples were refrigerated during transport and, within 72 h of collection, filtered in the laboratory (<0.45 μm) prior to analysis. Physical–chemical parameters, such as turbidity, suspended solids, and temperature, inorganic constituents, such as metals, and organic parameters, such as dissolved organic carbon (DOC) and ultraviolet absorbance (UVA), were analyzed as described in Dahm et al.⁷

Fluorescence excitation emission matrix (EEM) spectra were recorded for each sample using a Horiba FluoroMax 4 fluorometer (Edison, NJ, USA). Scans were conducted using excitation wavelengths from 240 to 450 at 10-nm steps,

emission wavelengths from 290 to 580 at 10-nm steps, 2-nm bandwidth, and 0.25-s integration time. The intensity of all EEM spectra was normalized by dividing the integrated intensity area of the Raman water curve at 350 nm wavelength excitation from the 370–450 nm emission wavelength range. Data analysis included a correction due to water-scattering by subtracting the signal of a blank milli-Q water sample analyzed under the same conditions. Three-dimensional contour plots were created by plotting fluorescence intensity as a function of emission (*x*-axis) and excitation (*y*-axis) wavelengths.

Five previously identified regions of maximum fluorescence, characteristic of specific organic components,¹³ were used to analyze the spectra: Region I (Aromatic proteins I): ex. 220–250, em. 280–332; Region II (Aromatic proteins II): ex. 220–250, em. 332–380; Region III (Fulvic acid-like): ex. 220–250, em. 380–580; Region IV (Microbial byproducts): ex. 250–470, em. 280–380; and Region V (Humic acid-like): ex. 250–470, em. 380–580 (SI Figure 1). Peaks from CBM produced water samples were characterized by these relative regions. In addition to peak locations, spectra were compared to one another statistically to determine the similarity between images. Percent similarity is defined as follows:

$$\text{percent similarity} = \left(1 - \frac{\sum \left| \frac{S_1}{S_{1,\text{max}}} - \frac{S_2}{S_{2,\text{max}}} \right|}{\text{Total}_{\text{pairs}}} \right) \times 100\%$$

where

S_1 = Spectrum matrix of sample 1

$S_{1,\text{max}}$ = Maximum intensity of the S_1 matrix wavelength pairs

S_2 = Spectrum matrix of sample 2

$S_{2,\text{max}}$ = Maximum intensity of the S_2 matrix wavelength pairs

Total_{pairs} = Total wavelength pairs in a spectrum matrix

EEM spectra unique to produced water samples were compared to a suite of water samples representing potential natural and anthropogenic sources of organic matter that may influence the EEM spectra of the wells. SI Table 2 describes the comparison samples, rationale for inclusion, and sample origin. These comparison sources include chemical well additives and hydraulic fracturing fluid to distinguish between anthropogenic and naturally occurring organic compounds. Shallow groundwater samples in the basins were not available, but surface water, brackish groundwater, and seawater samples were used to define baseline spectra. Brackish water samples were obtained from a shallow alluvial aquifer similar to overlying aquifers in the study basins as a comparison sample. Due to the high carbon content in the coal depositional environment, coal-derived organic matter is expected to be a visible contribution to the dissolved organic matter spectra. It is postulated that a significant portion of the organic signature in the CBM well EEM spectra is influenced by the highly organic coal environment from which the produced water is extracted.

To represent the organic signature from the coal itself, microcosm experiments were conducted in the laboratory under a variety of conditions to represent in situ coal to water ratios. For microcosm experiments, coal from wells drilled in the Powder River Basin was crushed and sieved with a U.S. standard wire mesh No. 5 sieve to achieve particle diameters of less than 4 mm. The coal was rinsed in deionized water and dried in an oven at 105 °C for 48 h. Preliminary

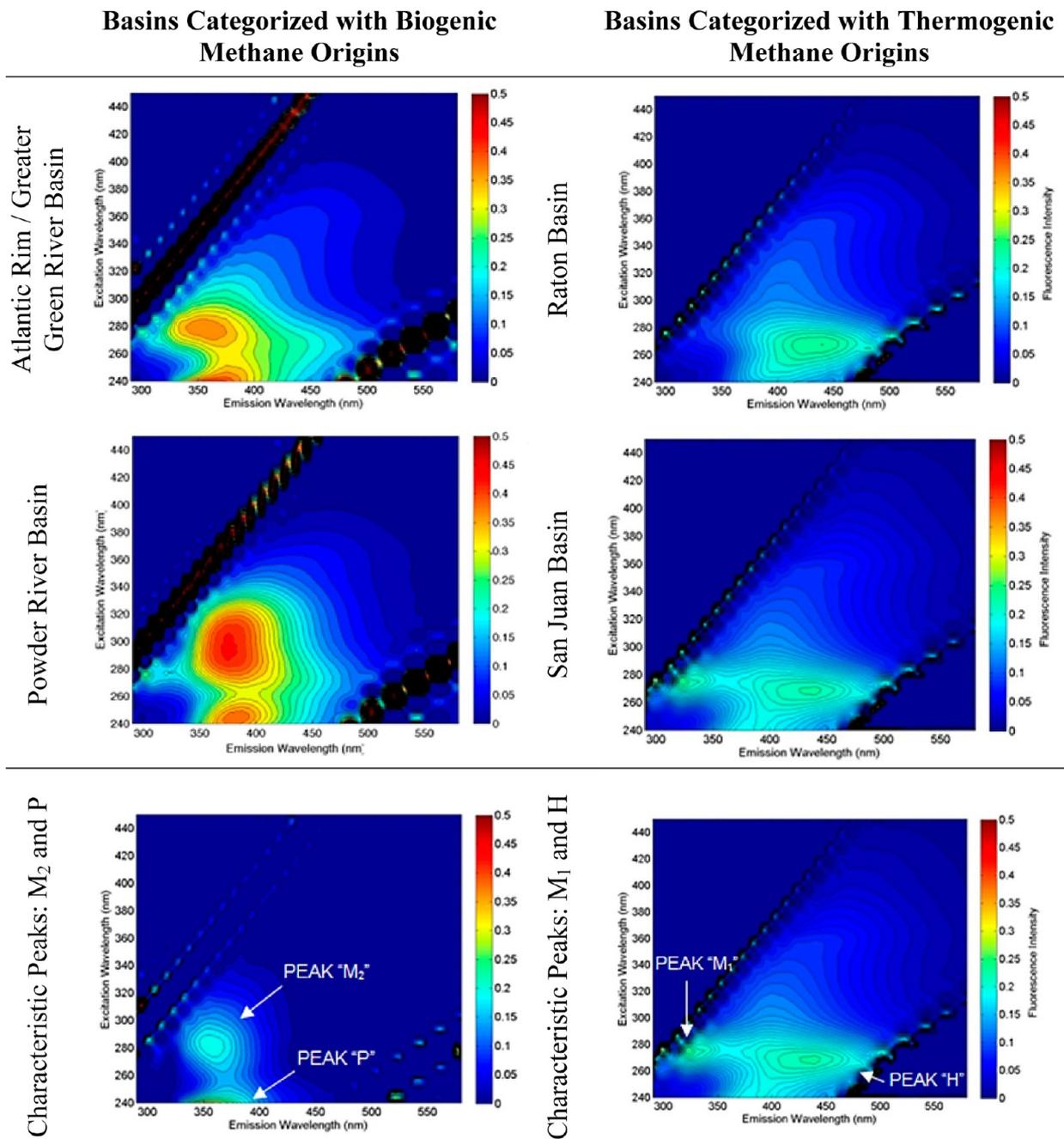


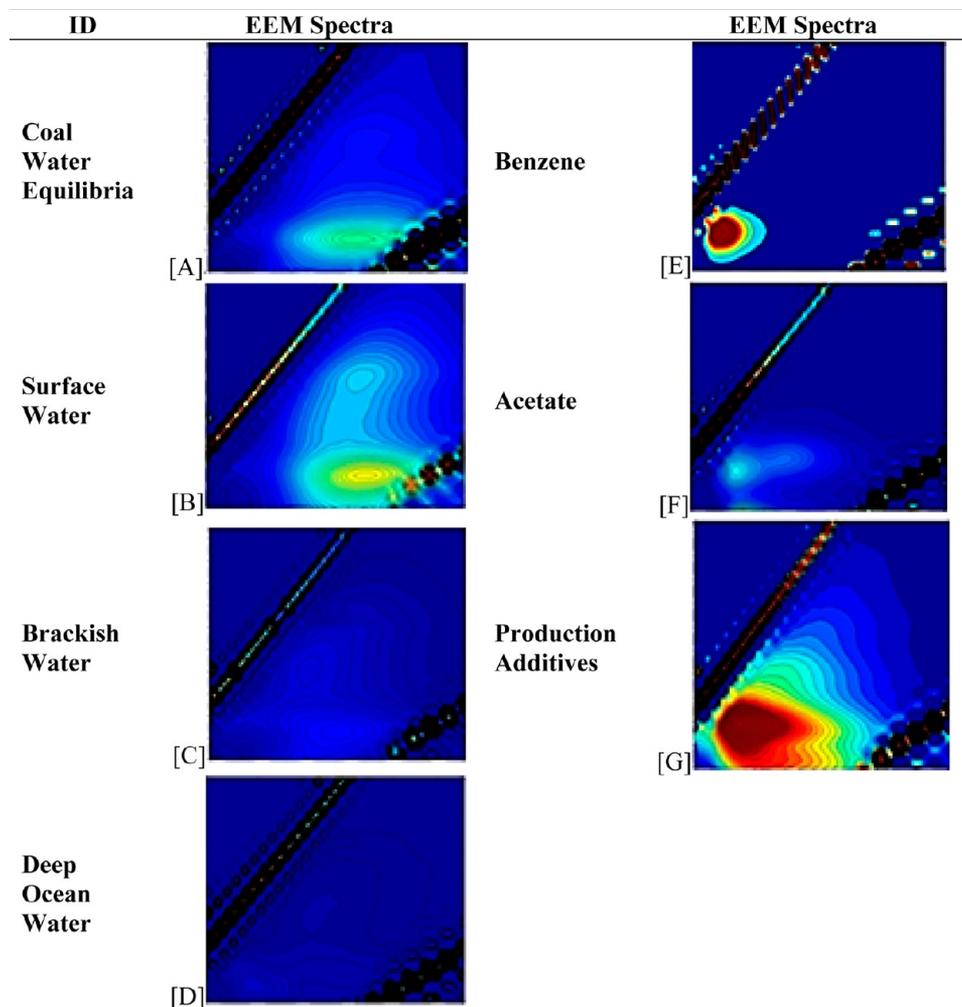
Figure 1. Representative excitation–emission matrix spectra from sampled CBM basins with similar spectra attributes and characteristic CBM produced water peaks. The spectrum displaying peaks M_2 and P, characteristic of the Atlantic Rim and Powder River basins, was created by subtracting the Raton Basin EEM spectra from the Atlantic Rim EEM spectra; the spectrum showing peaks M_1 and H, characteristic of the Raton and San Juan Basin is visible in the San Juan Basin Image.

experimentation revealed that an exposure period of 10 weeks was necessary to reach a target equilibrium DOC concentration of ~ 1.5 mg/L (representative of the produced water sample average DOC), with a coal to water ratio of 250 mg of coal to 60 mL of Milli-Q water. Sixty-milliliter amber glass bottles were filled to eliminate headspace, capped, and reacted for the 10-week period on a shaker table at room temperature. Each experiment was reproduced in triplicate and a blank solution (no coal) was reacted for the 10-week period with each test solution combination.

Inorganic constituents, specifically metals, also are present at higher relative concentrations in CBM produced water than in shallow alluvial groundwater.⁹ Studies investigating the effects

of metals in solution on fluorescence spectra suggest that trace metals that complex with organic matter can effectively quench the EEM spectra. These metals include copper, iron, nickel, and zinc.^{14,15} To study these potential inorganic interferences, coal microcosm experiments were conducted to test for isolated effects of metal concentrations on the EEM spectra and overall fluorescence intensity (OFI).

Samples from the coal–water equilibrium experiments were used to evaluate inorganic interferences in the EEM spectra. Experimental conditions included varying the types of metals present, which included individual tests for aluminum, barium, calcium, copper, iron, magnesium, manganese, nickel, strontium, and zinc at the 25th, 50th, and 75th percentile

Table 1. Comparison Sources for Coalbed Methane Produced Water EEM Spectra^a

^aNote: Spectra scales are x-axis excitation wavelengths from 240 to 450 at 10-nm steps, y-axis emission wavelengths from 290 to 580 at 10-nm steps, and fluorescence intensity ranging from 0 to 0.5 (blue to red).

concentrations observed for each metal in a regionally produced CBM produced water composite geochemical database.⁷ A reference list of the metal concentrations is available in SI Table 3. Metal chloride salts were used for the metal experiments. Each experimental protocol was reproduced in triplicate, and a blank solution (no coal) was reacted for the 10-week period with each test solution combination. After the experiments were completed, the amount of DOC produced by each microcosm, the 3-D fluorescence signature, and the pH were measured.

Methane is produced from both biogenic and thermogenic sources depending on the well formation environment and geologic history. Commercial biogenic coalbed gas reservoirs are mainly generated biologically with substrates used by microbes including organic compounds, CO₂, H₂, and acetate.¹⁶ Variations in access to oxygenated waters, nutrients, and micro-organisms are largely responsible for the extent of biodegradation of coal hydrocarbons.¹⁷ Secondary microbial gas and anaerobic biodegradation in reservoirs has an important impact on hydrocarbon quality¹⁸ and may also influence the organic signature in the EEM spectra.

To simulate wells actively generating methane, microcosms with the same Powder River Basin coal source inoculated with a Powder River Basin enrichment culture¹⁹ were analyzed with 3-

D fluorescence spectroscopy. In addition, high-performance liquid chromatography (HPLC) was performed on samples from microcosm incubations to detect organic acids in the liquid fraction. One milliliter of sample was extracted from the anaerobic serum bottles using a sterile 23-gauge needle and syringe. Liquid samples were filtered using a 0.22- μ m filter (Fisher, USA) prior to analysis. HPLC analyses were performed on an Agilent 1100 series instrument using a BioRad organic acid column. Organic acids were identified by comparing unknown samples to known standards containing succinic, oxalic, acetic, formic, and citric acids.

RESULTS

It is necessary to differentiate between groundwater naturally impacted by oil and gas formation hydrocarbons and groundwater supplies impacted by anthropogenic chemicals for fracturing and well production. Therefore, results presented focus on the characterization of the naturally occurring baseline 3-D fluorescence EEM spectra and the EEM spectra caused by the presence of anthropogenic compounds.

CBM Produced Water Spectra. The 111 CBM produced water samples collected in the field are characterized by generally low DOC concentrations averaging less than 2 mg/L in the basins studied. The EEM spectra generated from samples

in the Atlantic Rim and Powder River basins have peaks fluorescing primarily in Regions II and IV. These regions were previously characterized as aromatic proteins and microbial byproducts, respectively.¹³ Emission signals were also observed in the humic acid-like Region V at lower relative intensities than the rest of the spectra for these samples. Spectra from the 51 wells sampled in the Atlantic Rim and Powder River basins are consistent in peak signature across all the wells sampled (SI Figure 1).

The Raton and San Juan basin samples fluoresce primarily in the humic acid-like Region V (SI Figure 1). Samples from the Raton Basin and San Juan Basin are variable across basin wells, spanning from EEM spectra without measurable intensities to wells with OFI orders of magnitude higher than the samples in the Atlantic Rim and Powder River basins (SI Figure 2). Some of the Raton and San Juan samples exhibit small peaks at excitation wavelength of 270 nm and emission wavelength of 330 nm. A large high intensity peak in Regions II and IV resulting in an OFI of greater than 4000 is likely due to contamination from well drilling fluids. The elevated OFI is caused by a large peak in the EEM regions of excitation below 300 nm and emission below 450 nm overwhelming the total EEM spectra of these samples. These contaminated samples were observed as “foaming wells” during sampling due to a foaming additive used during well production. These wells exhibit similar to slightly higher DOC concentrations, between 1.5 and 4.5 mg/L for contaminated samples versus average DOC concentrations of 1.9 mg/L for uncontaminated samples. EEM spectra for contaminated samples exhibit a significantly higher OFI (greater than 4000 in most cases) than uncontaminated samples. Although the DOC of contaminated samples can be relatively similar, the EEM spectra and OFI easily identify contamination.

Representative EEM spectra from each basin are included in Figure 1. Representative spectra from each basin were compared to one another statistically to determine the similarity between spectra. The EEM spectra from the Atlantic Rim and Powder River basins are 97.3% similar, while representative EEM spectra from the Raton and San Juan Basins are 95.0% similar. When comparing across the four basins, the Atlantic Rim and Powder River basins are generally around 92.8% similar to the Raton and San Juan Basins, although visually the spectra appear different. EEM spectra subtraction was used to isolate four unique peaks specifically associated with each basin (Figure 1). Peak identifiers were given to the four peak locations. Peak P is in Region II where aromatic proteins dominate, Peaks M_1 and M_2 are in the region representative of microbial byproducts (region IV), and Peak H is in region V where humic acid-like organic matter dominates. The centroids of the four peaks are as follows: Peak P (ex. 240 nm, em. 375 nm), Peak M_2 (ex. 300 nm, em. 375 nm), Peak H (ex. 270 nm, em. 440 nm), and Peak M_1 (ex. 270 nm, em. 330 nm).

Peak M_2 and Peak P are uniquely associated with EEM spectra in the Atlantic Rim and Powder River basins. After subtracting the EEM spectra of the Raton and San Juan basins from the Atlantic Rim and Powder River basins, the resulting spectra isolate Peak M_2 and P as specific signatures and unique peaks (Figure 1), suggesting Peak H is present in all basins. Peak H dominates the EEM spectra of the Raton and San Juan basins, but is masked by Peaks M_2 and P in the Atlantic Rim and Powder River basins. Biogenic methane production is characteristic of the shallow coals of the Powder River Basin,²⁰

which increases the likelihood that microbial byproducts may contribute to the more complex signature (peaks M_2 and P) exhibited by these samples in region IV. Meanwhile, the more significantly thermogenic pathways in the Raton and San Juan basins result in spectra dominated by peaks M_1 and H with the distinct absence of peaks M_2 and P.

Comparison Spectra. Seven different comparison samples were used to determine whether the four EEM peaks observed in the CBM produced water samples could be linked to potential sources of organic matter found within the basins (Table 1 spectra A–G). All spectra were corrected to 1 mg/L DOC and the spectra were adjusted to a maximum fluorescence intensity of 0.5.

Coal–Water Equilibria: CBM produced water samples in all locations have a peak (H) in the same location as the equilibrated coal and aquifer water (Table 1, spectrum A). The Raton and San Juan Basin spectra are dominated by peak H, while samples from the Atlantic Rim and Powder River basins exhibit two additional peaks (M_2 and P) that are not present in the equilibrated coal–water samples.

Surface Water: Surface water from the Purgatoire River in the Raton Basin was characterized to determine whether the NOM signature in CBM produced water resembled that of surface water, reflecting potential recharge into the subsurface aquifer formations. The surface water signature had two peaks in region V (Table 1, spectrum B). The higher excitation and emission peak (ex. 360 nm, em. 470 nm) is not observed in any of the produced water samples, while the lower peak is similar to peak H in the produced water samples.

Formation Water: To determine whether coal seam formation water influences produced water NOM, brackish water and deep ocean water from sources not in contact with coal beds were scanned to provide comparison spectra. Both of these spectra had low DOC content (<0.4 mg/L) and minimal fluorescence intensity (Table 1, spectra C and D) in regions where the produced water samples were observed to have strong fluorescence. Results from these spectra indicate that formation water is unlikely to contribute to the observed CBM produced water spectra.

Benzene: Benzene was detected in select samples from both the Raton Basin and San Juan Basin. Benzene fluoresces in the EEM spectrum at an excitation of 270 nm and emission of 330 nm (Table 1, spectrum E), similar to the P Peak in the produced water samples. Benzene was not detected in any of the Powder River or Atlantic Rim basin samples, but the presence of benzene in Raton and San Juan basin samples correlates with the occurrence of peak P. Benzene is a potential byproduct of thermogenic methanogenesis.¹⁰

Acetate: Acetate is an organic intermediate substrate for acetoclastic methanogenesis and is potentially present in basins with biogenic methane, such as the Powder River Basin.^{21,22} The acetate EEM spectrum is comparable to peaks M_2 and P present in the Powder River and Atlantic Rim basin samples (Table 1, spectrum F). Inoculated microcosms actively producing methane also generate spectra with peaks M_2 and P. Additionally, samples with higher M_2 and P peak intensities correlate to higher acetate concentrations (Figure 2). This is consistent with coal incubations from other studies in which acetate was produced and consumed during the course of methane production.²³ Although produced water samples from these basins were not analyzed for discrete organic compounds, acetate is an organic intermediate in the anaerobic biodegradation of coal to methane under laboratory conditions

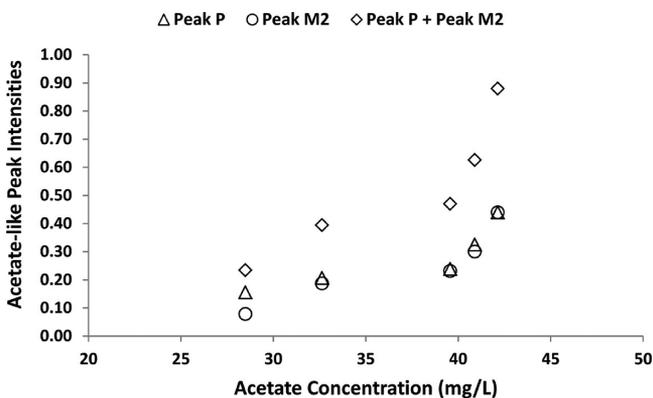


Figure 2. Comparison of acetate concentration in biologically active methane producing coal microcosms to peaks P and M₂ observed in biologically active coalbed methane EEM spectra.

and has been detected in formation water samples from coalbed methane basins.^{21,24}

Chemical Additives: Lastly, anthropogenic sources were analyzed for fluorescence patterns to distinguish between anthropogenic and natural sources of organic matter in the system. Chemical additives used during well production and hydraulic fracturing produce distinct fluorescent signatures. Friction reducer, a foaming agent, produces a signature with high relative intensity compared to CBM produced water spectra (Table 1, spectrum G). The samples from the Raton and San Juan basins suspected of well contamination due to foaming during sampling (SI Figure 2, maximum for the Raton and San Juan basins) exhibit an EEM spectrum similar to the friction reducer.

Interferences with the EEM Spectra. The absence of well-defined spectra was noted in certain Raton and San Juan Basin samples with DOC at concentrations expected to fluoresce. Spectra absence was hypothesized to be due to quenching by metals present in solution. In coal–water

equilibrium microcosms, EEM spectra displayed similar peak locations to peak H, but at varying intensities depending on the presence and concentration of certain metals. Iron, copper, nickel, and zinc all exhibit quenching effects, with iron and copper eliminating the EEM spectra image to an OFI less than 100 (Figure 3). Nickel and zinc show quenching effects at the 75th percentile concentrations, while aluminum, barium, calcium, magnesium, manganese, and strontium did not significantly impact the OFI. The Raton and San Juan basin samples contain higher metal concentrations than the Powder River and Atlantic Rim basins. Absence of spectra in the Raton and San Juan basins is related to higher relative iron and copper concentrations in these samples quenching the EEM. Peak quenching in the Atlantic Rim and Powder River basins was not observed in the field samples collected.

DISCUSSION

Van Voast suggests that produced water from CBM wells exhibits characteristics unique to the originating coal formation.⁶ Therefore, this discussion section focuses on the classification of naturally occurring organic signatures in CBM wells using the 3-D fluorescence EEM spectra and anthropogenic chemical compounds added during well production or hydraulic fracturing.

Classifying Well Types. Current knowledge of EEM spectra of organic matter occurring in CBM produced water is limited, particularly over the extent of the basins and wells sampled for this study. The EEM spectra generated during this study revealed a qualitative fingerprint of the types of NOM present in CBM produced water. Table 2 characterizes produced water based on fluorescence spectra attributes observed in this study. In general, CBM produced water is characterized by DOC concentrations below 5 mg/L. The 3-D fluorescence EEM spectra created from CBM samples produced unique peaks that relate to specific attributes from each CBM basin. For example, the EEM spectra from CBM

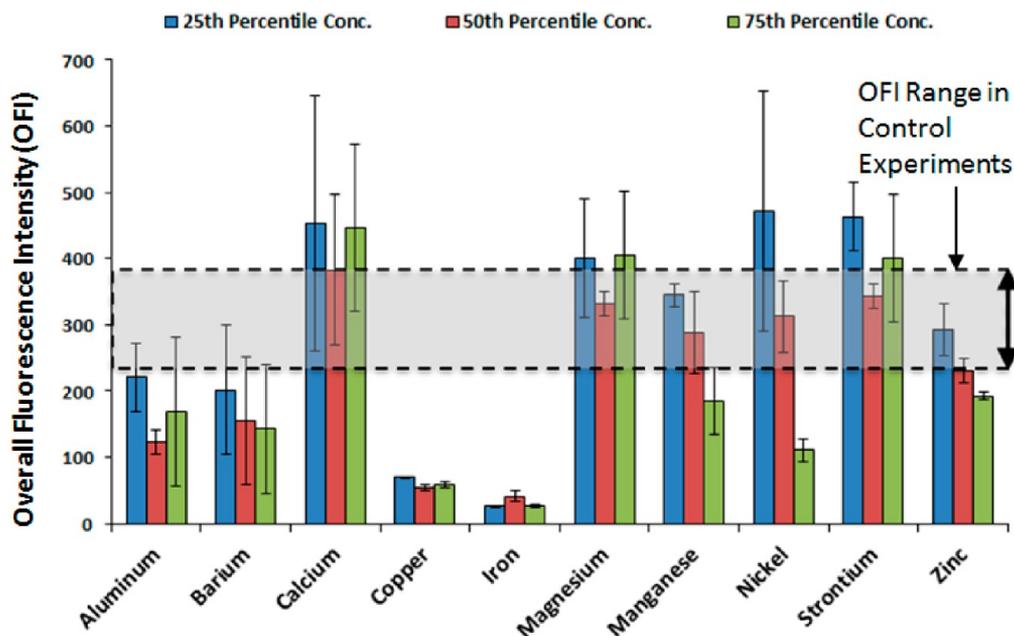
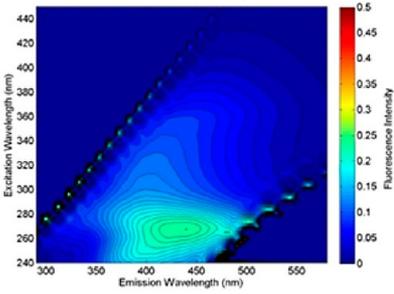
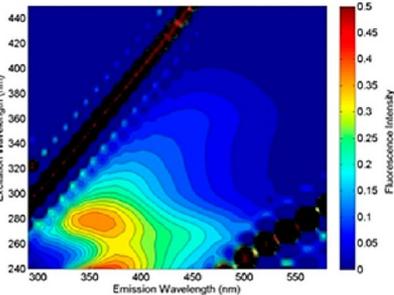
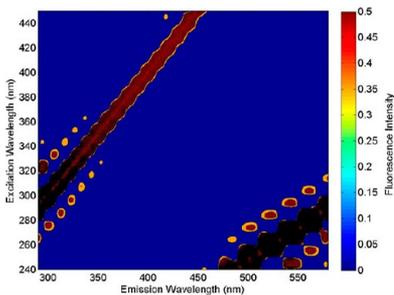
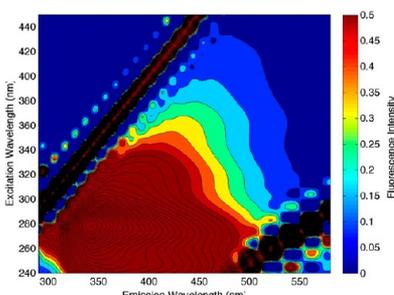


Figure 3. Resulting overall fluorescence intensity (OFI) measurements of EEM spectra from coal–water equilibria experiments conducted in the presence of metals and concentrations observed in the produced water samples.

Table 2. Characterization of Produced Water Using Fluorescence Spectroscopy^a

Representative Spectra Classification	Spectra Characteristics
<p>Natural Coal-water Equilibria Signature</p> 	<p>Fluorescing Region:</p> <ul style="list-style-type: none"> - Region V: ex. 250–470, em. 380–580 - Humic acid-like <p>Dominant Peak:</p> <ul style="list-style-type: none"> - Peak H (ex. 270 nm, em. 440 nm) <p>Notable absence of peaks:</p> <ul style="list-style-type: none"> - Peak P (ex. 240 nm, em. 375 nm) - Peak M₂ (ex. 300 nm, em. 375 nm)
<p>Naturally Occurring Biologic Activity</p> 	<p>Fluorescing Regions:</p> <ul style="list-style-type: none"> - Region II: ex. 220–250, em. 332–380 - Aromatic proteins II - Region IV: ex. 250–470, em. 280–380 - Microbial by-products - Region V: ex. 250–470, em. 380–580 - Humic acid-like <p>Dominant Peaks:</p> <ul style="list-style-type: none"> - Peak P (ex. 240 nm, em. 375 nm) - Peak M₂ (ex. 300 nm, em. 375 nm)
<p>Metal Interferences</p> 	<p>Notable absence of peaks:</p> <ul style="list-style-type: none"> - Peak P (ex. 240 nm, em. 375 nm) - Peak M₂ (ex. 300 nm, em. 375 nm) - Peak H (ex. 270 nm, em. 440 nm) <p>Overall Fluorescence Intensity (OFI):</p> <ul style="list-style-type: none"> - Less than 100 with DOC > 0.5 mg/L
<p>Well Production/Hydraulic Fracturing Chemicals</p> 	<p>Notable flooding of peaks:</p> <ul style="list-style-type: none"> - Peak P (ex. 240 nm, em. 375 nm) - Peak M₁ (ex. 270 nm, em. 330 nm) - Peak M₂ (ex. 300 nm, em. 375 nm) - Peak H (ex. 270 nm, em. 440 nm) <p>Overall Fluorescence Intensity (OFI):</p> <ul style="list-style-type: none"> - Greater than 4,000 with DOC > 5.0 mg/L

^aNote: Spectra scales are x-axis excitation wavelengths from 240 to 450 at 10-nm steps, y-axis emission wavelengths from 290 to 580 at 10-nm steps, and fluorescence intensity ranging from 0 to 0.5 (blue to red).

produced water exhibit a signal that comes from interactions between coal and the aquifer in all basins.

In addition, the Powder River and Atlantic Rim basins both exhibit two peaks in similar locations to the two peaks created by acetate. The similarity to acetate suggests these peaks may be indicative of biogenic methanogenesis in these basins. Conversely the absence of peaks M₂ and P potentially suggest the absence of biogenic methane pathways in the Raton and San Juan Basin samples. Primary or secondary microbial gas generation mixing with thermogenic methane already in place in the reservoir can cause complicated isotopic signatures.¹⁸ Although these signatures are more complex than the Raton and San Juan basin spectra, the organic matter is naturally occurring. These baseline signatures are important to reduce

the risk of falsely identifying aquifer contamination by anthropogenic additives.

With regards to anthropogenic contamination, a number of studies have focused upon the risks of natural gas production on drinking water aquifers. EEM spectra have been used to understand the vulnerability of aquifers to contamination and are useful when defining protection areas.¹¹ This study shows that EEM spectra provide an excellent tool for the identification of chemicals used in hydraulic fracturing and chemical additives used in well production. Synthetic polymers produce distinct peaks within the EEM spectrum with OFI higher than expected for CBM produced water not containing these constituents (Table 1, spectrum G and Table 2). The presence of chemical additives in drinking water aquifers or discharge water bodies of these types of organic chemicals used in fracturing and well

production is readily identifiable through the use of 3-D fluorescence spectroscopy, which offers a relatively simple analytical characterization method to detect contamination from gas operations.

■ ASSOCIATED CONTENT

● Supporting Information

Additional information on the study basins, metal concentrations used for the microcosm experimental conditions, definitions for the five characteristic fluorescing regions on EEM spectra, ranges of observed EEM spectra within each basin, and further discussion on additional applications for using 3-D fluorescence spectroscopy in coalbed methane produced water research. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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