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Dissolved organic matter fluorescence within oil and gas produced water from U.S. unconventional petroleum plays: Comparisons and consequences for beneficial reuse

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Produced water (wastewater generated during petroleum extraction) frequently contains elevated concentrations of dissolved organic matter due to the close association with organic-rich source rocks, expelled petroleum, and organic additives used during hydraulic fracturing of unconventional reservoirs. High salinities common in produced water (up to 10x seawater salinity) and the complex dissolved organic matter (DOM) matrix create both analytical and treatment challenges for characterizing and beneficially reusing produced water. Assessing DOM fluorescence provides an opportunity to survey a wide range of oil and gas wastewater compositions which can inform treatment plans that protect environmental health. Excitation-emission matrix spectroscopy (EEMS) can rapidly characterize the fluorescent component of DOM with minimal interference from matrix effects. We applied EEMS to evaluate the DOM composition in 18 produced water samples from six North American unconventional petroleum plays. Represented reservoirs include the Eagle Ford Shale (northern Gulf of Mexico basin), Wolfcamp/Cline Shales (Permian basin), Marcellus Shale and Utica/Point Pleasant Shale (Appalachian basin), Niobrara Chalk (Denver-Julesburg basin), and the Bakken Formation (Williston basin). EEMS spectra and DOM concentrations were measured, gas-oil-ratios (GOR) were mined from IHS Markitâ„¢, and total dissolved solids (TDS) concentrations were previously published by other studies or measured. Results indicate that the relative chromophoric DOM composition in produced water from unconventional reservoirs may distinguish petroleum thermal maturity (e.g., heavy oil vs. dry gas) but is generally insensitive to TDS and total DOM concentration. EEMS Fluorescence Regional Integration of regions traditionally defined as the more aromatic humic acid and fulvic acid-like DOM indicate an inverse relationship between the integrated fluorescence and the gas-oil-ratio (GOR) of the producing well. Based on this preliminary EEMS produced water survey, there is an opportunity to utilize EEMS analysis to elucidate DOM aromatic structure, inclusion of heteroatoms, and the recalcitrance of DOM. From interpreted DOM structural information, operators and regulators may more accurately predict potential impacts of DOM on treatment processes and the environment upon beneficial reuse.