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Subsurface Halogenation of Hydraulic Fracturing Fluid Additives

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Produced water is the largest waste stream associated with hydraulic fracturing of unconventional oil and gas wells. The presence of toxic organic contaminants in produced water prevents it from being reused for agriculture, livestock watering, or municipal use. Instead, the water is often disposed of as toxic waste in subsurface disposal wells, which increasingly cause induced seismicity. An improved understanding of the identity, concentrations, and toxicities of organic contaminants in the water would help water treatment facilities apply targeted purification techniques to produced water, enabling its reuse.

Many produced water contaminants are transformation products—compounds that are generated during the fracturing process by chemical reactions between injected chemicals and reservoir components. Reactions between fracturing fluid additives, reservoir brine, and injected oxidants result in halogenation reactions which generate halogenated contaminants with high expected toxicity. This study builds off the work of Burrows et al. (Earth and Space Chemistry, 2023), wherein the influence of dissolved iron on halogenation of a model fracturing fluid additive in simulated hydraulic fracturing brine was studied. Here, we report an analysis of produced water field samples from the Marcellus shale region, with a focus on identifying halogenated compounds.

Produced water samples originated from an oil and gas wastewater treatment facility in the Marcellus Shale region and were analyzed using LC-QTOF-MS (Agilent 1290/6520) and GC-MS (Agilent 6890/5975). Organic compounds were extracted from the samples through solid phase extraction prior to LC-QTOF-MS analysis and through liquid-liquid extraction prior to GC-MS analysis. LC-QTOF-MS data was processed using MassHunter combined with HaloSeeker 2.0 (Leon et al., Analytical Chemistry, 2019). GC-MS data analysis was performed using ChemStation, and compounds were putatively identified using the NIST spectral library.

LC-QTOF-MS and GC-MS analysis provides complementary information regarding non-volatile and semi-volatile hydrophobic and hydrophilic organics present in produced water. Using LC-QTOF-MS, surfactant-based analytes such as LAEs, as well as transformation products like PEGs and PEG derivatives, were putatively identified. Using GC-MS, semi-volatile compounds as aliphatic hydrocarbons, phthalates, glycol derivatives, hydrocarbons, and halogenated compounds were putatively identified. Results obtained from this research will assist in determining whether a treated produced water would be suitable for non-disposal use.