

Inherent Biodegradability of Organic Chemicals used in Hydraulic Fracturing Fluid

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Well completion methods known as hydraulic fracturing inject approximately 15 million L of a water-based solution containing up to 15% proppant and up to 1% chemicals into subsurface rock formations to stimulate production of oil and gas wells. In the Pennsylvania Marcellus shale, around 1.7 million L of injected fluid per well return to the surface as produced water, regionally generating a few billion liters of hypersaline, chemically complex, potentially hazardous fluid waste for storage, transport and treatment.

Little is known of the attenuation of chemical mixtures created for hydraulic fracturing within treatment systems or the natural environment. A synthetic hydraulic fracturing fluid was developed from commonly used commercial additives. Laboratory experiments evaluated the inherent biodegradation potential of the fluid mixture as a sole substrate by monitoring removal of dissolved organic carbon (DOC) from solution by activated sludge microorganisms. Experiments were conducted across a range of substrate concentrations (25 to 200 mg/L DOC) and salinities (0 to 60,000 mg/L TDS) to test individual and combined effects of these factors on microbial toxicity and biodegradation rates. Substrate removal was coupled to biomass production using flow cytometry to estimate microbial growth kinetics.

An average $70\% \pm 2\%$ DOC loss occurred within 7 days at both dilute and field-representative starting concentrations, with biodegradation rates up to $0.51 \pm 0.02 \text{ d}^{-1}$. Analysis of volatile and semivolatile organics in solution suggests microorganisms preferentially degrade n-alkane hydrocarbon chains and lower molecular weight substituted and unsubstituted VOCs (e.g., BTEX, THMs). Approximately $30\% \pm 2\%$ of added DOC remains in solution after one week, including high molecular weight semivolatile hydrocarbons ($>300 \text{ Da}$), suggesting that a sizeable portion of organic additives are initially resistant to microbial transformation, and may persist in treatment systems or the natural environment. The combined effect of high DOC and high salinity completely inhibited degradation of hydraulic fracturing fluid.