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Indications of Transformation Products from Hydraulic Fracturing Additives in Shale Gas Wastewater

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Unconventional natural gas development (UNGD) generates large volumes of wastewater, whose detailed composition must be known for adequate risk assessment and treatment. In particular, there is a need to elucidate the structures of organic chemical additives, extracted geogenic compounds, and transformation products. This study investigated six Fayetteville Shale UNGD wastewater samples for their organic composition using purge-and-trap gas chromatography-mass spectrometry (P&T-GC-MS) in combination with liquid-liquid extraction with comprehensive two-dimensional gas chromatography-time of flight-mass spectrometry (GCxGC–TOF-MS). Following application of strict compound identification confidence criteria, we classified compounds according to their putative origin. Samples displayed distinct chemical distributions composed of typical geogenic substances (hydrocarbons), disclosed UNGD additives (e.g., hydrocarbons, phthalates, such as diisobutyl phthalate, and radical initiators, such as azobisisobutyronitrile), and undisclosed compounds (e.g., halogenated hydrocarbons, such as 2-bromohexane or 4-bromoheptane). Undisclosed chloromethyl alkanoates (chloromethyl propanoate, pentanoate, and octanoate) were identified as putative delayed acids (those that release acidic moieties only after hydrolytic cleavage, whose rate could potentially be controlled), suggesting they were deliberately introduced to react in the subsurface. Identification of halogenated methanes and acetones, in contrast, suggested they were formed as unintended by-products. Our study highlights the possibility that UNGD operations generate transformation products, knowledge of which is crucial for risk assessment and treatment strategies, and underscores the value of disclosing potential precursors that are injected into the subsurface.