



# Temporal dynamics of halogenated organic compounds in Marcellus Shale flowback

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## ABSTRACT

The chemistry of hydraulic fracturing fluids and wastewaters is complex and is known to vary by operator, geologic formation, and fluid age. A time series of hydraulic fracturing fluids, flowback fluids, and produced waters was collected from two adjacent Marcellus Shale gas wells for organic chemical composition analyses using ultrahigh resolution mass spectrometry. Hierarchical clustering was used to compare and extract ions related to different fluid ages and many halogenated organic molecular ions were identified in flowback fluids and early produced waters based on exact mass. Iodinated organic compounds were the dominant halogen class in these clusters and were nearly undetectable in hydraulic fracturing fluid prior to injection. The iodinated ions increased in flowback and remained elevated after ten months of well production. We suggest that these trends are mainly driven by dissolved organic matter reacting with reactive halogen species formed abiotically through oxidizing chemical additives applied to the well and biotically via iodide-oxidizing bacteria. Understanding the implications of these identified halogenated organic compounds will require future investigation in to their structures and environmental fate.

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## 1. Introduction

Halogenated organic compounds (HOCs) have been recently identified in shale gas wastewaters using both targeted and non-targeted analytical approaches (Hoelzer et al., 2016; Luek et al., 2017; Maguire-Boyle and Barron, 2014). Furthermore, HOCs are of particular interest because they are not known additives used in the hydraulic fracturing process and although a handful of mechanisms have been proposed, their origin remains unknown (Hoelzer et al., 2016; Luek et al., 2017; Maguire-Boyle and Barron, 2014). The environmental fate and toxicity of these compounds also remains unknown.

Non-targeted ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) is widely used to investigate the chemical composition of diverse organic matter

based on its high mass accuracy and resolution (Dvorski et al., 2016; Gonsior et al., 2011; Kellerman et al., 2014; Roullier-Gall et al., 2015; Walker et al., 2014). This approach has been applied to complex natural and engineered systems to describe compositional changes not understood *a priori* and without the use of hundreds or thousands of costly analytical standards (Chen et al., 2016; Gonsior et al., 2016; Lavonen et al., 2013; Shakeri Yekta et al., 2012; Sleighter et al., 2014). Ultrahigh resolution FT-ICR-MS operated in negative mode is an appropriate approach for identifying unknown deprotonated HOCs including diverse disinfection by-products (DBPs) (Gonsior et al., 2015; Lavonen et al., 2013; Luek et al., 2017; Xu et al., 2013). Paired with solid phase extraction (Dittmar et al., 2008), FT-ICR-MS is uniquely suited for describing the temporal dynamics of diverse HOCs found in high salinity shale gas wastewater.

Understanding the behavior of HOCs within an individual hydraulic fracturing well is essential for narrowing down their possible origins and environmental fate. HOCs have been hypothesized to be transformation products (Hoelzer et al., 2016; Luek et al., 2017), but time series data have not been used previously to investigate this possibility. Therefore, the aim of this study was to track changes to

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the dissolved organic matter (DOM) pool of Marcellus Shale gas well fluids over the first ten months of well operation. Specifically, we combined solid phase extraction with FT-ICR-MS and used hierarchical clustering analysis to identify key shifts in the distribution of HOCs and suggest plausible formation mechanisms.

## 2. Methods

Hydraulic fracturing fluid, flowback fluid, and produced water samples were collected from two adjacent hydraulic fracturing wells at the Marcellus Shale Energy and Environment Laboratory (MSEEL) field site in Morgantown, WV (Fig. S1) between November 2015 and September 2016 (Carr, 2017). DOM was solid phase extracted from water samples and analyzed using FT-ICR-MS. Hierarchical clustering analyses were performed on the resulting ions and assigned molecular formulas to track the temporal trends of HOCs.

### 2.1. Sample collection

MSEEL wells MIP-3H and MIP-5H (herein referred to as 3H and 5H) were sampled from a gas-fluid separator in autoclaved high-density polyethylene carboys from the separator outlet. Fluid was then transferred in to 1L base-washed low-density polyethylene containers using a peristaltic pump, minimizing headspace. Samples were collected approximately daily during the initial week of flowback (December 2015, fluid production rates as high as 1000 barrels  $\text{d}^{-1}$ ), bi-weekly for the following 3 months (early production water, fluid production rates 10s of barrels  $\text{d}^{-1}$ ), monthly for 3 months, and then bimonthly (late production water, fluid production rates very low,  $\sim 1$  barrel  $\text{d}^{-1}$ ) (mseel.org). On certain dates, the 5H well was not producing fluid so no sample was collected. Samples were refrigerated at 4 °C and shipped on ice within two weeks of collection. One field blank was collected by taking MilliQ water in to the field and then processed in the same manner as samples.

### 2.2. Extraction of Organic Compounds

Upon receipt, samples were filtered over a 0.7  $\mu\text{m}$  glass fiber filter (Whatman GF/F) in to glass bottles previously baked at 500 °C. Filtered samples (200 mL) for solid phase extraction were immediately acidified to pH 2 with concentrated hydrochloric acid and extracted over 1 g/6 mL Bond Elut PPL solid phase extraction cartridges (preconditioned with 2 cartridge volumes of methanol followed by 2 volumes of 0.1% formic acid solution) (Dittmar et al., 2008). Loaded cartridges were desalted using a 200 mL dilute hydrochloric acid rinse (pH = 2) followed by a 30 mL 0.1% formic acid solution rinse to avoid halide contamination of the methanolic extract. Large volume washing of cartridges reduces the likelihood of iodo-adducts (Luek et al., 2017; Xu et al., 2013) and prior investigations with high and ultrahigh resolution electrospray mass spectrometry have confirmed covalently-bound iodine in complex mixtures (Luek et al., 2017; Moulin et al., 2001; Xu et al., 2013). Cartridges were dried under vacuum and eluted with 10 mL ultrapure methanol. Methanolic extracts were stored at  $-20$  °C prior to FT-ICR-MS analysis.

### 2.3. FT-ICR-MS analysis

Methanolic extracts were diluted 1:5 in ultrapure methanol and injected at 120  $\mu\text{L hr}^{-1}$  using a Bruker Solarix 12T electrospray ionization FT-ICR-MS located at the Helmholtz Zentrum Munich, Germany. The instrument was operated in negative mode to target solid phase extracted compounds and HOCs. Complementary positive ionization was not performed although this mode could have

ionized additional organic compounds, including nitrogen containing HOCs. 500 scans were averaged for each sample and a post calibration was performed using a list of known DOM internal calibrants to obtain a mass accuracy of less than 0.1 ppm (Table S1). The obtained full scan mass resolution was better than 400,000 at  $m/z$  400, allowing for precise formula assignments (Hertkorn et al., 2008). All  $m/z$  ions identified in the field blank were removed prior to further processing. Following the methods of Sleighter et al. (2012), replicate sample mass spectra were compared to confirm that variability in the mass spectral analysis across samples was different from variability among extraction replicates as a function of the % of overlapping  $m/z$  ions and a regression of peak magnitudes from two replicates (Figs. S2 and S3).

Because the ions of interest were not understood *a priori*, no surrogate or internal standards were added to samples prior to extraction or analysis, and hence why FT-ICR-MS is used as a semi-quantitative approach. Ion suppression issues caused by changes in the matrix were limited by diluting samples sufficiently as determined by the transient spectra. However, remaining extraction and ionization efficiency issues are not addressed using this non-targeted approach. For this reason, changes that would only be consistent with the expected changes in the matrix itself (i.e., consistently present in only unbroken fracturing fluids but absent in all flowback and produced waters, the largest contrast in the fluid matrices) were not discussed to limit false pattern identification.

### 2.4. Hierarchical cluster analysis

Hierarchical cluster analysis was performed using Gene Cluster 3.0 and TreeView on log transformed ion abundances to limit clustering driven only by high intensity ions. Clustering analysis using average linkages was performed on uncentered  $m/z$  ions identified in each well on ions present in 2 or more samples between  $m/z$  150–400 (3H,  $n = 6613$ ; 5H,  $n = 5296$ ). Clusters were selected with ions unique to flowback and early produced waters (first three months of well operation) and assigned formulas.

### 2.5. Formula assignments

Molecular formulas were assigned to individual ions from the entire spectra including selected hierarchical clusters using in-house software (Hertkorn et al., 2008). A range of 150–700  $m/z$  was selected to encompass the majority of ions in the spectra and where the calibration is reliable to 0.1 ppm. Formulas were assigned with a maximum value per assignment of  $\text{C}_{100}\text{H}_{\infty}\text{O}_{80}\text{N}_3\text{S}_2\text{Cl}_3\text{Br}_3\text{I}_3$  and a maximum error of 0.2 ppm. The mass error associated with ions identified below the lowest molecular weight calibrant was sufficient for formula assignment in this 0.2 ppm window. Nonsensical formula assignments were removed using a number of criteria in favor of alternative plausible formula assignments. Formulas not passing the nitrogen rule (McLafferty and Turecek, 1993) were removed within this software and remaining assignments were further reduced to remove invalid formulas by removing those with an oxygen to carbon ratio (O/C) greater than one or a negative double bond equivalent (DBE). Raw values of formulas containing only carbon, hydrogen, and oxygen (CHO), as well as nitrogen (CHON) or sulfur (CHOS) between  $m/z$  150–700 are reported in Fig. S4.

Additional filtering of assigned formulas identified during the cluster analysis involved removing assignments with more than 3 heteroatoms (e.g.,  $\text{CHOI}_3$  kept,  $\text{CHOI}_3\text{S}_1$  removed) and preferentially removing duplicate assignments with very low O/C ratios and higher heteroatoms based on consistencies found when checking

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