Temporal Toxicity in Hydraulic Fracturing Wastewater from Black Shale Natural-Gas Wells Influenced by Production Times and Chemical Additives

Mina Aghababaei[1], Jenna L Luek[1], Paul F Ziemkiewicz[2], Paula J Mouser[1]
[1]Department of Civil and Environmental Engineering, University of New Hampshire
[2]West Virginia Water Research Institute, West Virginia University

University of New Hampshire
College of Engineering and Physical Sciences

Abstract

The process of extracting hydrocarbon resources from low permeability formations such as black shales using horizontal drilling and hydraulic fracturing techniques is increasingly utilized around the globe. The hydraulic fracturing process generates large volumes of wastewater fluids known as flowback and produced waters (FPW). FPW contains a wide range of organic and inorganic constituents derived from both xenobiotic and geogenic origin, including known toxicants. Here, we assess the toxicity of 42 input media and produced fluid samples collected from four wells in the Utica Formation and Marcellus Shale using two distinct endpoint tests. Broad spectrum toxicity was assessed using a BioLuminescence Inhibition Assay employing the halotolerant bacterium *Aliivibrio fischeri,* while human cytotoxicity was evaluated using a N-acetylcysteine (NAC) thiol reactivity assay. The acute toxicity and thiol reactivity of early-stage flowback was higher than later produced fluids, with levels diminishing through time as the natural gas wells matured. These data show that both acute toxicity and cytotoxicity persists in produced waters up to nine months after hydraulic fracturing, with toxicity levels heavily influenced by specific well additives, as opposed to sample fraction or shale formation.

Aims and Hypotheses

The goal of the present study is to assess the toxicity of FPW samples on ecosystem and human health using BLIA and NAC thiol assay.

Hypothesis:
1. There is a decrease in toxicity with time after hydraulic fracturing
2. There is no difference in toxicity between replicate wells or shale formations
3. Removal of sediments and associated hydrophobic organic matter and metals decrease the toxicity
4. There is no toxicity in the input media

Site

Samples were collected from four hydraulically fractured natural-gas wells in the northern Appalachian Basin: two from the Utica-Point Pleasant Formation (Utica-6 and Utica-7) and two from the Marcellus Shale (Marcellus-4 and Marcellus-5).

Marcellus-4:
n= 10 flowback and produced water (FPW), 1 kill fluid, 1 drill mud, and 1 sidewall mud
Marcellus-5
n= 8 FPW
Utica-6:
n= 9 FPW, 2 freshwater tank, 1 produced water additive, and 1 recycled produced water additive
Utica-7:
n= 8 FPW

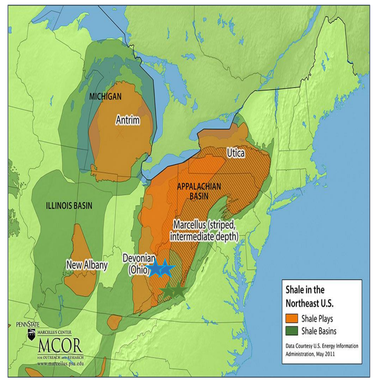


Figure 1. Marcellus and Utica outlines

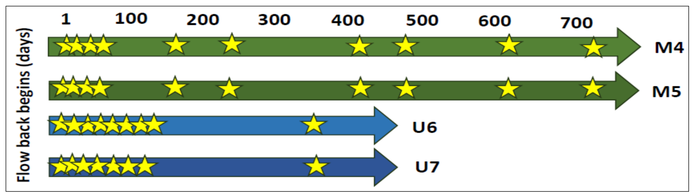


Figure 2. Marcellus and Utica formations time-series points selected to perform the BioLuminescence Inhibition Assay and NAC thiol assay analyses

References

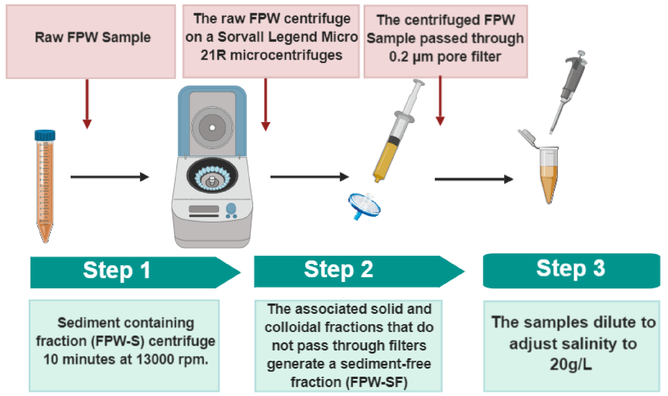
1. ISO 11348-3, 2008 Determination of Inhibitory Effect of Water Samples on the Light Emission of *Vibrio fischeri* (luminescence bacteria test)
2. Abbas, Mazhar, et al. "Vibrio fischeri bioluminescence inhibition assay for ecotoxicity assessment: A review." *Science of the Total Environment* 626 (2018): 1295-1309.

Methodology

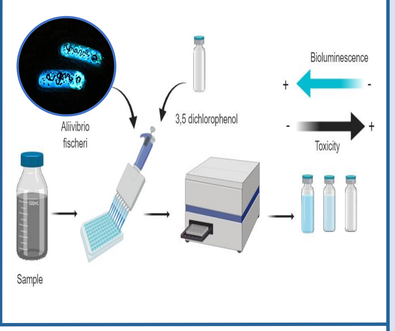
Aliivibrio fischeri Applications

- Complex effluents
- Surface water
- Ground water
- Dye wastewater from the textile industry
- White-water and effluent from paper mills
- Municipal waste effluent and sediments

FPW Sample Preprocessing

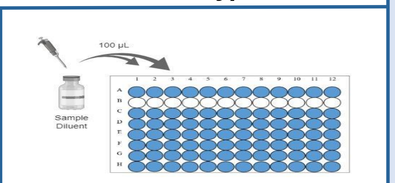


Aliivibrio fischeri inhibition test is a very sensitive, cost effective, and easy to operate bioassay, requiring only 5-30 min to predict toxicity based on ISO Standard 21338. A microplate reader is used to measure the BioLuminescence of *Aliivibrio fischeri* bacteria (formerly *Vibrio fischeri*). Toxic contaminants cause inhibition of *Aliivibrio fischeri* Bioluminescence.

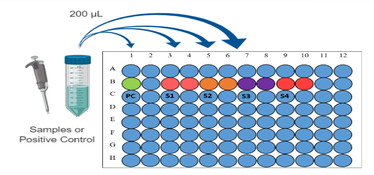


BLIA (BioLuminescence Inhibition Assay) Procedure

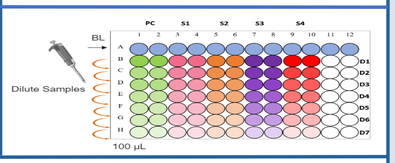
100 µL of Sample Diluent dispensed into all wells of the microplate **EXCEPT ROW B**.
ROW A is used for non-treated bacteria (negative control) and provides background levels of Bioluminescence production.



200 µL of positive control (PC) is transferred to well 1B.
200 µL of each prepared sample stock transferred to the appropriate wells in **row B**, starting from **column 3**.



100 µL of sample or control from the first well pipetted in the column to the well below. This transfer sequence repeated for every well in the column.



N-acetyl-L-cysteine (NAC) Thiol Reactivity Assay

The N-acetylcysteine (NAC) thiol reactivity assay is an essential predictor of additive toxicity for human and ecological health. The cysteine thiols (-SH), is a cellular pathway that addresses exposure to toxins in the biological systems.

Results

Fig.3 Controls and Input Medias

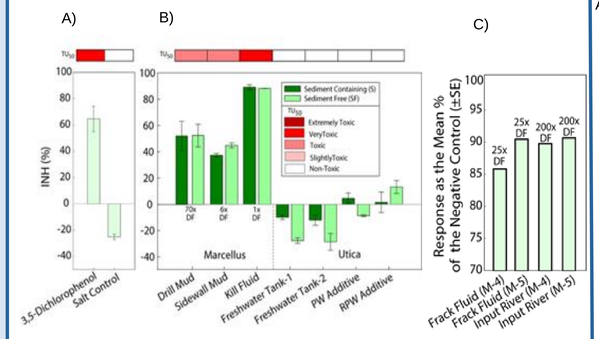


Figure 3. Average acute toxicity of (A) positive control (3,5-Dichlorophenol, 6.8 mg/l) and salt control and (B) input media from the Marcellus and Utica well pads, measured using the *Aliivibrio fisheri* assay. (C) NAC thiol reactivity results for input media from the Marcellus well pads.

Fig.4 Aqueous Chemistry Trends

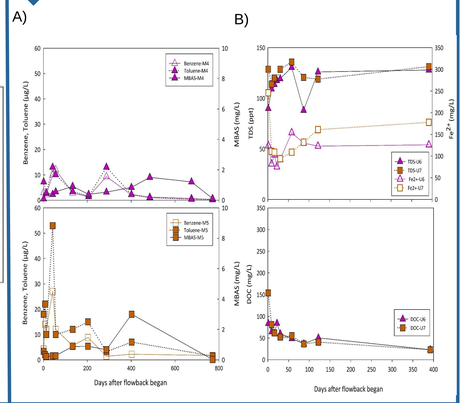


Figure 4. (A) Benzene, Toluene and MBAS trends in the Marcellus Shale, (days 1-771) (B) TDS, Fe2+ and DOC trends in the Utica Shale, (days 1-392).

Fig.5 Flowback and Produced Water

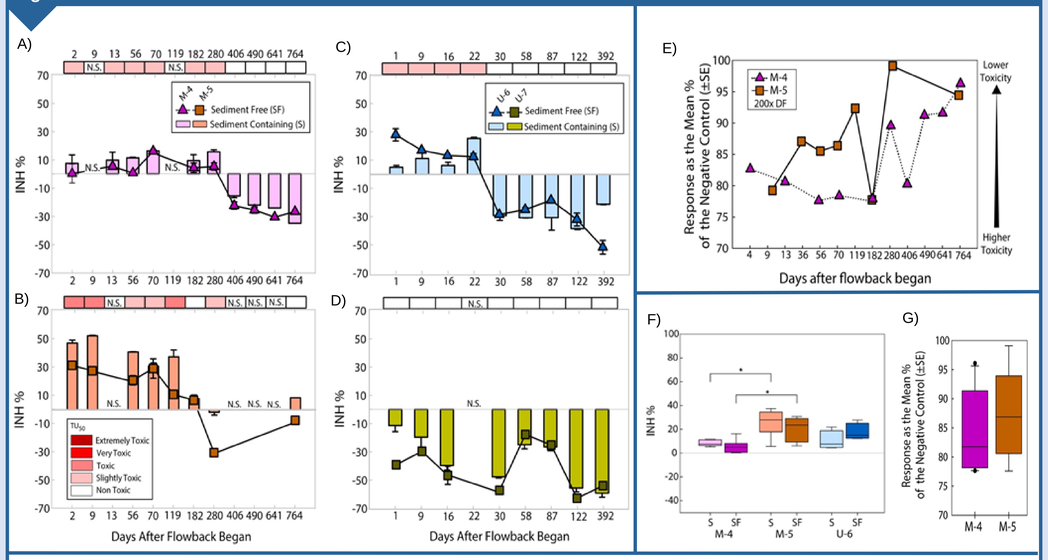


Figure 5. BioLuminescence Inhibition Assay results for flowback and produced water from Marcellus Shale natural-gas wells M-4 (A) and M-5 (B) as well as Utica natural gas wells (U-6 (C) and U-7 (D). Sediment containing samples are depicted as bars while sediment-free samples are shown as lines with markers. Boxes above each figure represents toxicity unit classification (TU_{50}) based on EC_{50} values determined from assay concentrations. (E) NAC thiol reactivity results for flowback and produced water from Marcellus Shale natural-gas wells M-4 and M-5. (F) Average acute toxicity of FPW samples and (G) Average NAC thiol reactivity of FPW samples.

- The acute toxicity and thiol reactivity of early-stage flowback was higher than later produced fluids, with levels diminishing through time as the natural gas wells matured.
- Differences in toxicity between paired natural gas well samples were associated with specific chemical additives and their concentrations.
- Samples containing a larger diversity and abundance of organic additives resulted in higher acute toxicity, while samples having a higher composition of diammonium peroxidisulphate, a strong oxidizer, showed greater thiol reactivity.
- These data show that both acute toxicity and cytotoxicity persists in produced waters up to nine months after hydraulic fracturing.

Acknowledgements

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