Temporal Toxicity in Hydraulic Fracturing Wastewater from Black Shale Natural-Gas Wells in the Appalachian Basin

Mina Aghababaei, Jenna L. Luek, Paul F. Ziemkiewicz Paula J. Mouser

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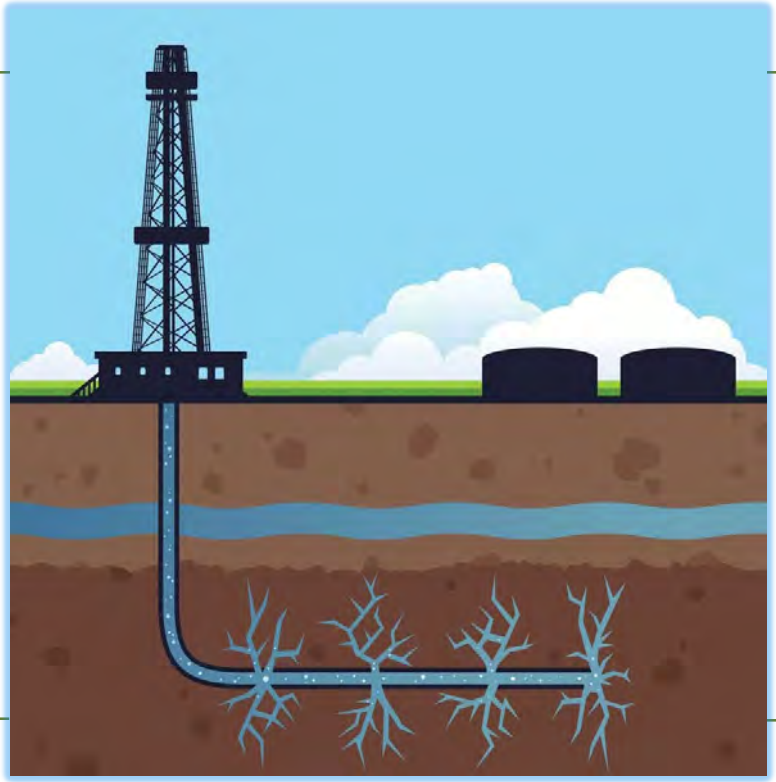
CBET Award # 1823069

Outline

1. Research Motivation
2. Research Methods
3. Sample Collection
4. Results
5. Conclusion

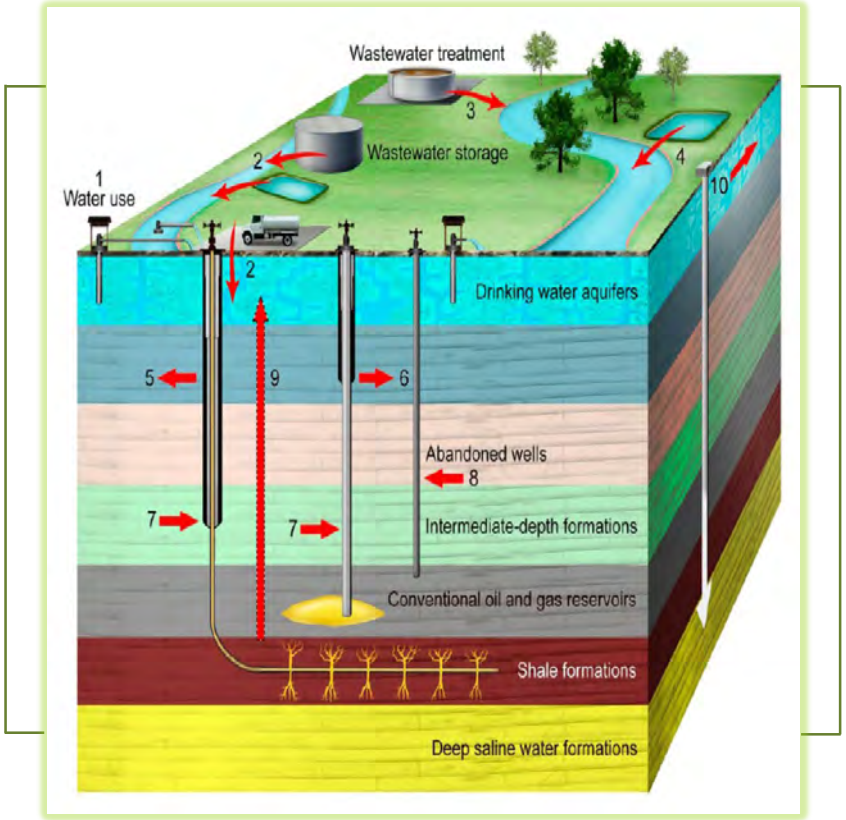
What is Hydraulic Fracturing?



https://www.motherearthnews.com/

- Hydraulic fracturing is an oil and gas well development process that typically involves injecting water, sand, and chemicals under high pressure into a bedrock formation via the well (USGS).

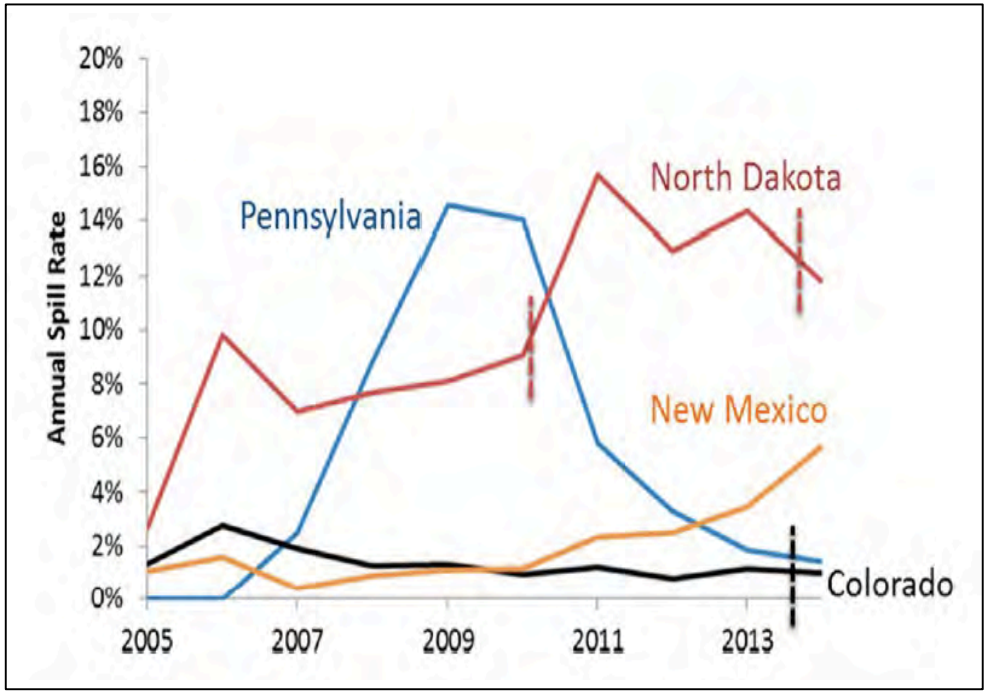
Research Motivation



Vengosh et al., 2014 (ES & T)

- Amount of water use for hydraulic fracturing (average reported **water usage** per well include: Marcellus Shale, Pennsylvania, 4.5 million gallons)
- Large volume of flowback and produced water (FPW) (7.95×10^8 m^3 of FPW was produced from 2005 to 2014 in the U.S)
- FPW spills into aquatic environment (surface and groundwater contamination)
- FPW disposal

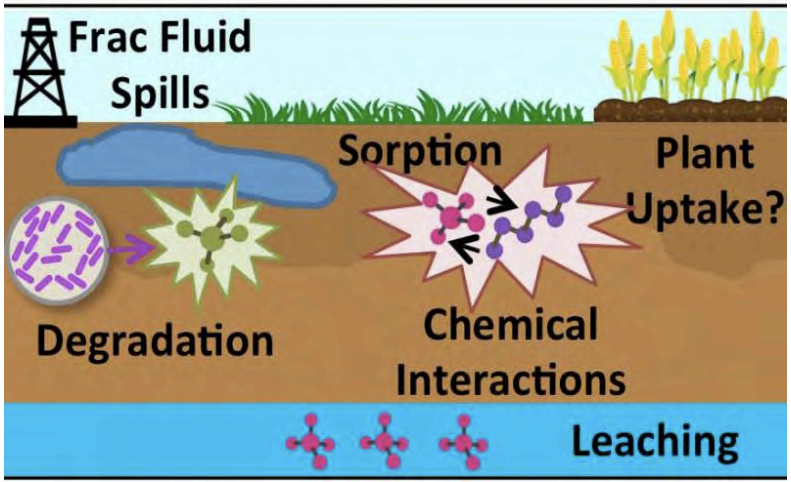
Research Motivation



Patterson et al., 2017 ES&T

- Fracking fluid spills occur frequently.
- Between 2005 and 2014 there were 6648 spills reported across the four states.
- North Dakota: 4453 spills
- Pennsylvania: 1293 spills
- New Mexico: 426 spills
- Colorado: 476 spills
- Most spills from storing and moving fluids

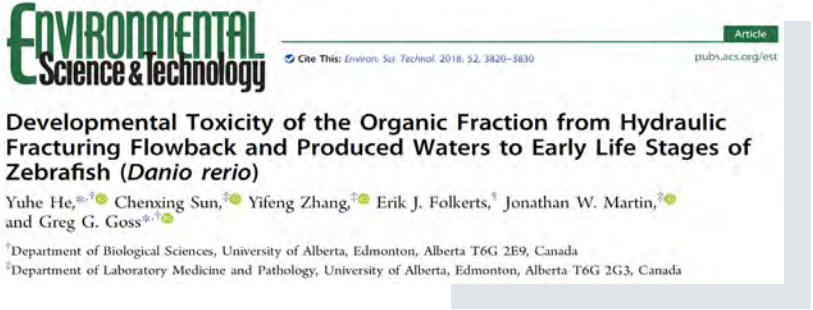
Research Motivation



McLaughlin et al., 2016

- Hydraulic fracturing chemicals during spills may have varying fates.
- Injected fluids are generally, composed of proppants such as ceramic beads and sand, biocides, gelling and foaming agents, pH adjustors, clay stabilizers, and surfactants
- Knowledge is very limited regarding the possible toxicological impact of FPW spills on human and ecosystem health.

Research Motivation



Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2018, 52, 3820−3830

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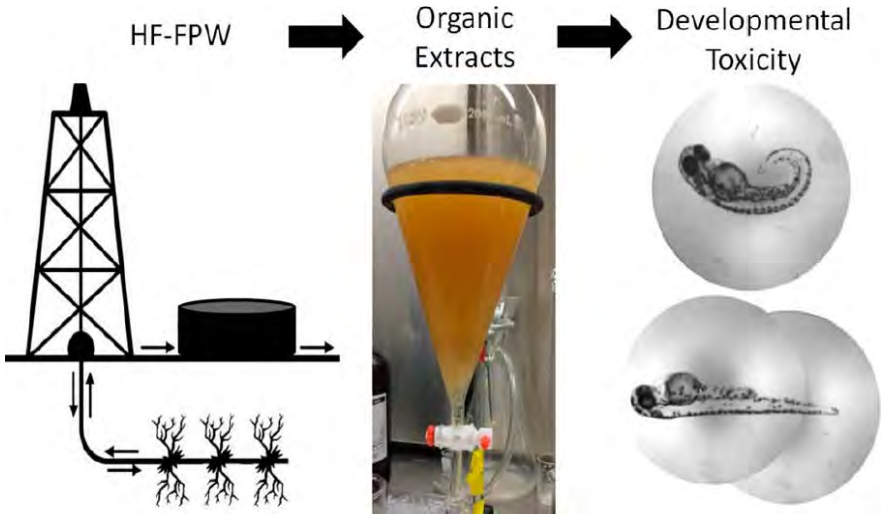
Developmental Toxicity of the Organic Fraction from Hydraulic Fracturing Flowback and Produced Waters to Early Life Stages of Zebrafish (*Danio rerio*)

Yuhe He,*[,†] Chenxing Sun,[‡] Yifeng Zhang,[‡] Erik J. Folkerts,[†] Jonathan W. Martin,[‡] and Greg G. Goss*[,†]

[†]Department of Biological Sciences, University of Alberta, Edmonton, Alberta T6G 2E9, Canada

[‡]Department of Laboratory Medicine and Pathology, University of Alberta, Edmonton, Alberta T6G 2G3, Canada

- Assess the effects of FPW on zebrafish embryos exposed to various organic fractions extracted from two different FPW samples
- Adverse effects in developing zebrafish embryos.
- **Salt content** is the major lethal component in acute toxicity.



Research Motivation

Environmental Science & Technology

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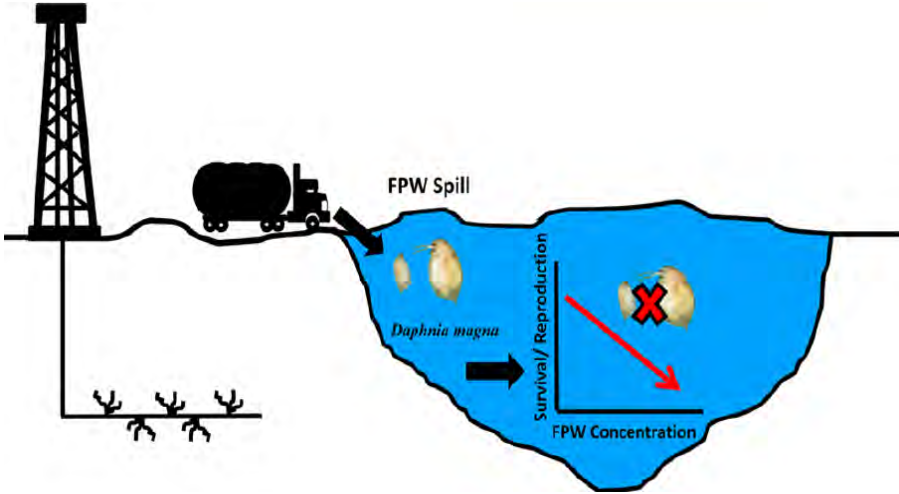
Sublethal and Reproductive Effects of Acute and Chronic Exposure to Flowback and Produced Water from Hydraulic Fracturing on the Water Flea *Daphnia magna*

Tamzin A. Blewett,[*,†,∥] Perrine L. M. Delompré,[†,∥] Yuhe He,[†] Erik J. Folkerts,[†] Shannon L. Flynn,[‡] Daniel S. Alessi,[‡] and Greg G. Goss[†,§]

[†]Department of Biological Sciences, University of Alberta, Edmonton, Alberta T6G 2R3, Canada
[‡]Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2R3, Canada
[§]National Institute for Nanotechnology, 11421 Saskatchewan Drive, Edmonton, Alberta T6G 2M9, Canada

- Assess the toxicity of both whole FPW and combinations of key FPW components on *Daphnia magna*
- Organic fraction
- **Salt components**

are the key mediators of acute mortality.



Research Motivation

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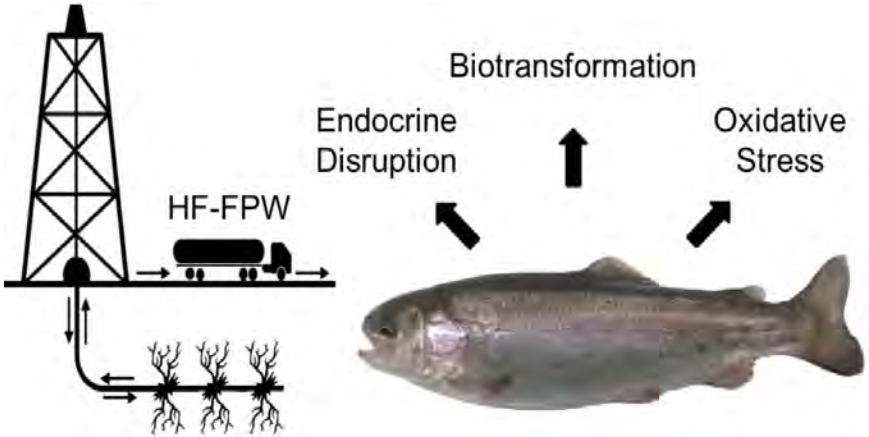
Effects on Biotransformation, Oxidative Stress, and Endocrine Disruption in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Hydraulic Fracturing Flowback and Produced Water

Yuhe He,[†,#] Erik J. Folkerts,[†,#] Yifeng Zhang,[‡] Jonathan W. Martin,[‡] Daniel S. Alessi,[§] and Greg G. Goss[*,†]

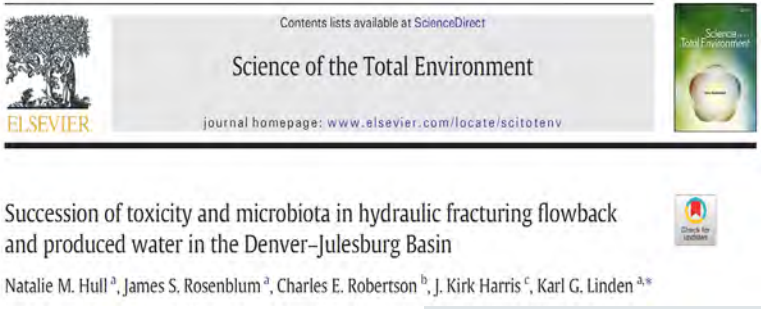
Evaluate the adverse effects of Sediment containing, sediment free fraction of FPW and activated charcoal treated on Rainbow Trout

- Organic contaminants
- **Sediment**

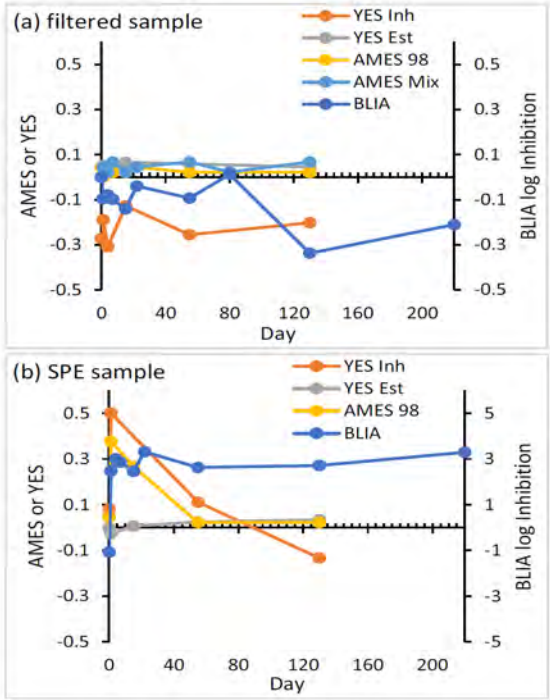
are important components in causing adverse effects related to biotransformation and oxidative stress pathways.



Research Motivation



- Cytotoxicity of FPW was measured via BLIA
- Toxicity of FPW was greatest the first day of flowback, and declined within the first 1–2 months of flowback
- Toxicity remained high for the first 220 days of flowback as measured by BLIA in 25× SPE concentrated samples.



Time-series flowback and produced water (days1–220) (a) 0.45 µm filtration of samples (b) solid phase extraction (25× concentration).

General toxicity of saline media can be assessed with *Aliivibrio fischeri*

FEMS Microbiology Ecology, 92, 2016, fiw166
doi: 10.1093/femsec/fiw166
Advance Access Publication Date: 8 August 2016
Minireview

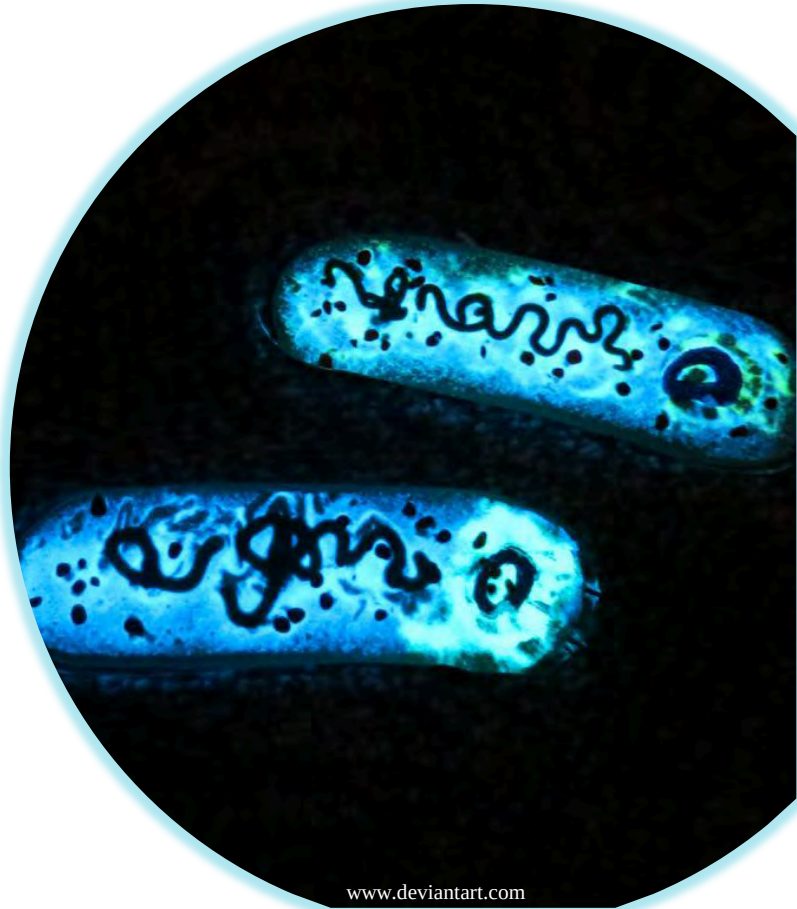
MINIREVIEW

Hydraulic fracturing offers view of microbial life in the deep terrestrial subsurface

Paula J. Mouser[1,*], Mikayla Borton[2], Thomas H. Darrah[3], Angela Hartsock[4] and Kelly C. Wrighton[2]

- *Aliivibrio fischeri* is a halotolerant bacteria that exists in hydraulically fractured natural-gas wells.

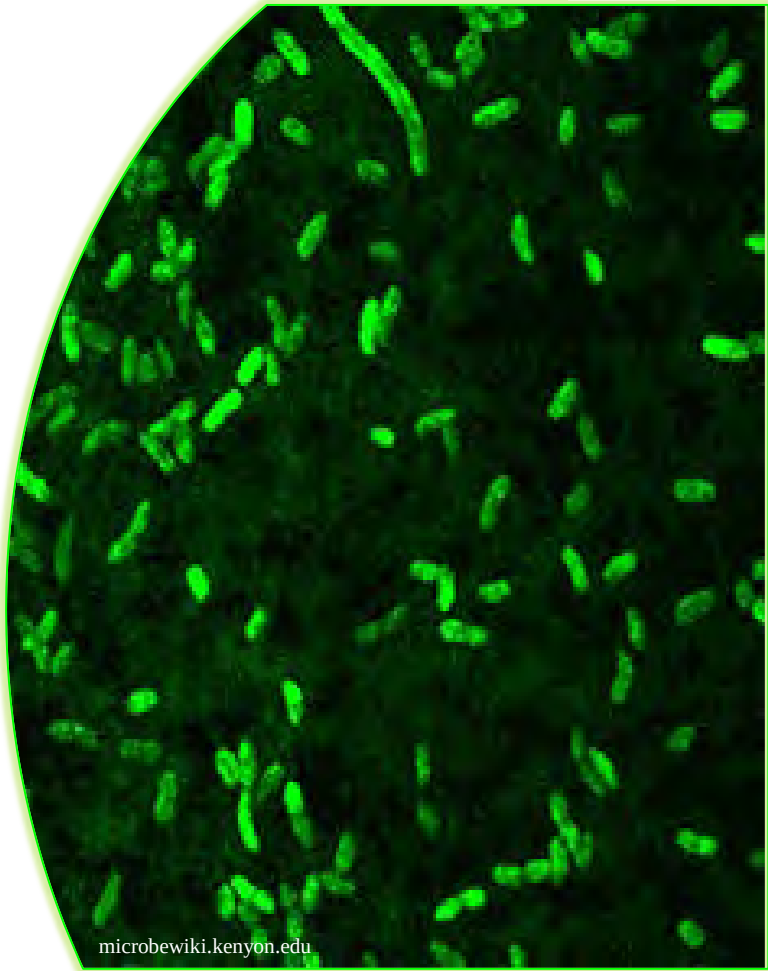
- We used Lumoplate Ultimate Matrix kit, EBPI, ON, Canada.



www.deviantart.com

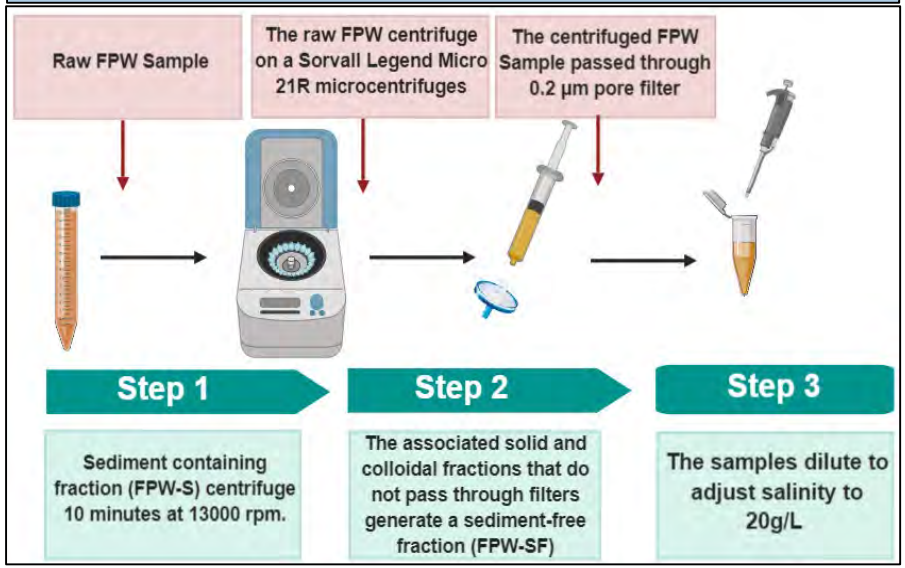
BLIA for assessing general toxicity in saline FPW media

- BLIA is an appropriate bioassay for determining inhibitory effects in high salinity suspensions of FPW samples.
- High sensitivity to a broad range of environmental contaminants compared to other bacterial assays.
- Applicable to a wide range of samples, including complex effluents.

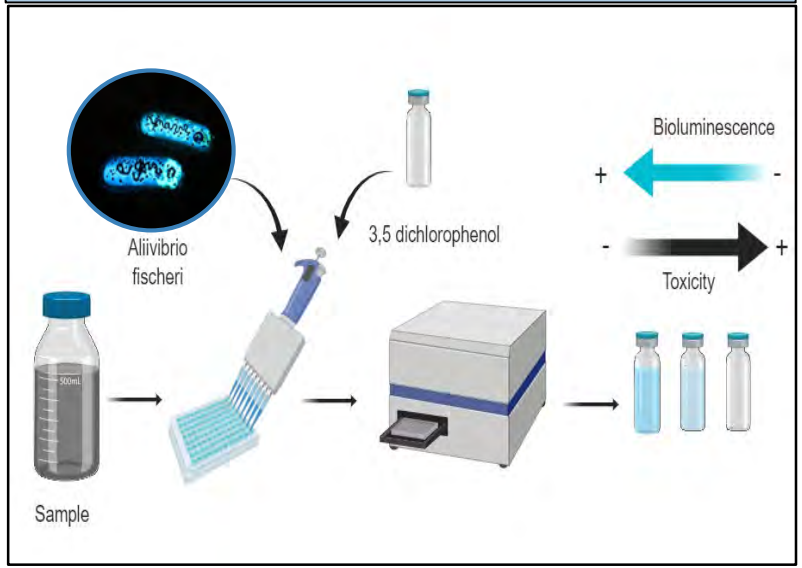


Sample Pre-processing and Microassay Procedure

FPW Sample Processing



BLIA Procedure



Research Motivation

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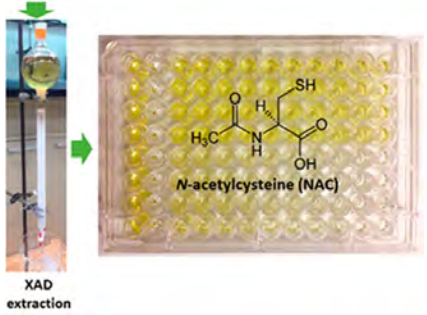
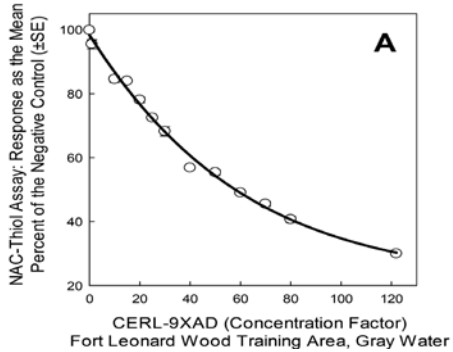
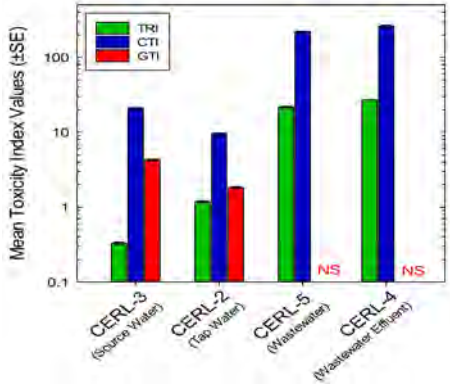
Thiol Reactivity Analyses To Predict Mammalian Cell Cytotoxicity of Water Samples

Shengkun Dong,[†,‡] Martin A. Page,[∥] Elizabeth D. Wagner,[§,⊥] and Michael J. Plewa*[§,⊥]

[†]Department of Civil and Environmental Engineering, [‡]Department of Crop Sciences, and [⊥]Safe Global Water Institute, University of Illinois at Urbana−Champaign, 1101 West Peabody Drive, Urbana, Illinois 61801, United States
[§]US Army Engineer Research and Development Center, 2902 Newmark Drive, Champaign, Illinois 61822, United States







Comparison of the average toxicity index values of thiol reactivity (TRI), cytotoxicity (CTI), and genotoxicity (GTI) from concentrated water and wastewater samples.

- Develop and calibrate an in chemico NAC-based thiol reactivity assay.
- Analyze a series of source, drinking, and wastewaters using this assay.

Environmental Science & Technology
Article
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pubs.acs.org/est

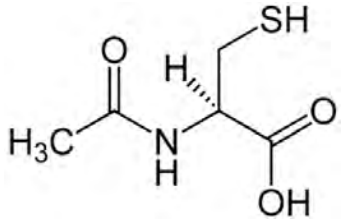
Toxicological Comparison of Water, Wastewaters, and Processed Wastewaters

Shengkun Dong,[†,‡,⊥] Martin A. Page,[¶] Nedal Massalha,[†,⊥,□] Andy Hur,[¶] Kyu Hur,[§,⊥] Katherine Bokenkamp,[§,⊥] Elizabeth D. Wagner,[§,⊥] and Michael J. Plewa*[§,⊥]

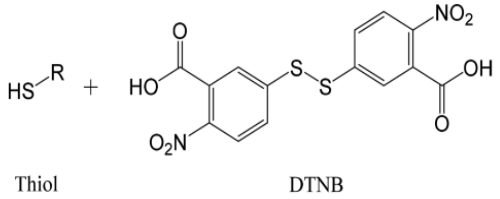
NAC Thiol Reactivity Assay

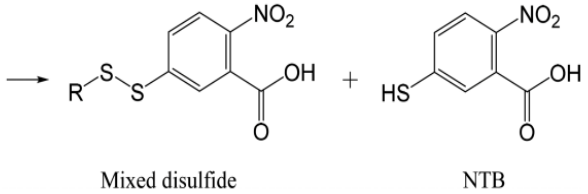
- The N-acetylcysteine (NAC) thiol reactivity assay is an essential predictor of additive toxicity for human and ecological health

- The cysteine thiols (-SH), is a cellular pathway that addresses exposure to toxins in the biological systems.



Chemical structure of *N*-acetyl-L-cysteine

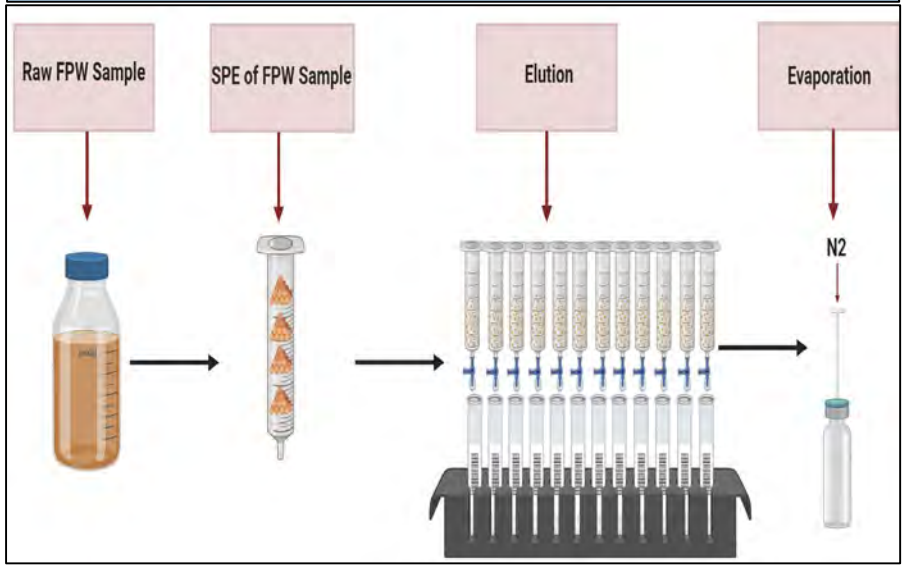




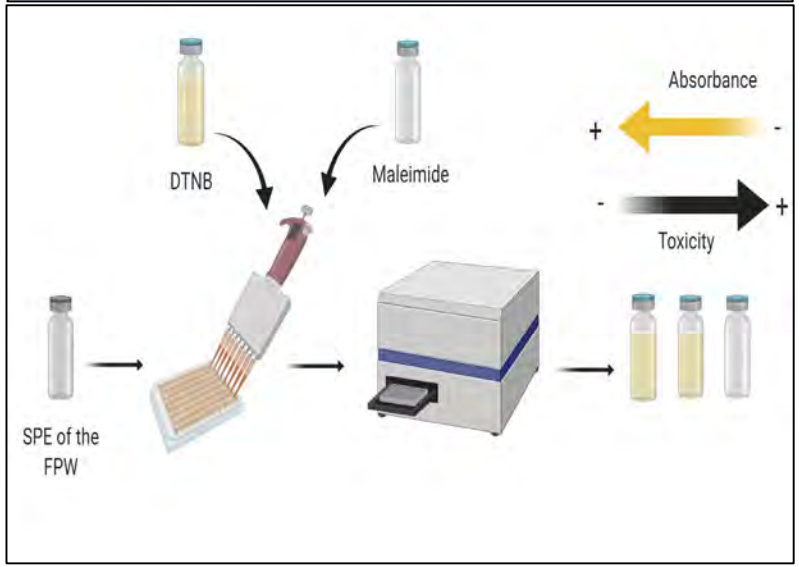
The reaction of Ellman's reagent with a thiol group (Dong et al., 2018).

Sample pre-processing and microassay procedure

FPW Sample Processing



NAC thiol Assay Procedure



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.

Sample Collection

Marcellus-4
n= 10 flowback and produced water (FPW),
Input media :1 kill fluid, 1 drill mud, and 1 sidewall mud

Marcellus-5
n= 8 FPW

Utica-6
n= 9 FPW,
Input media: 2 freshwater tank, 1 produced water additive, and 1 recycled produced water additive

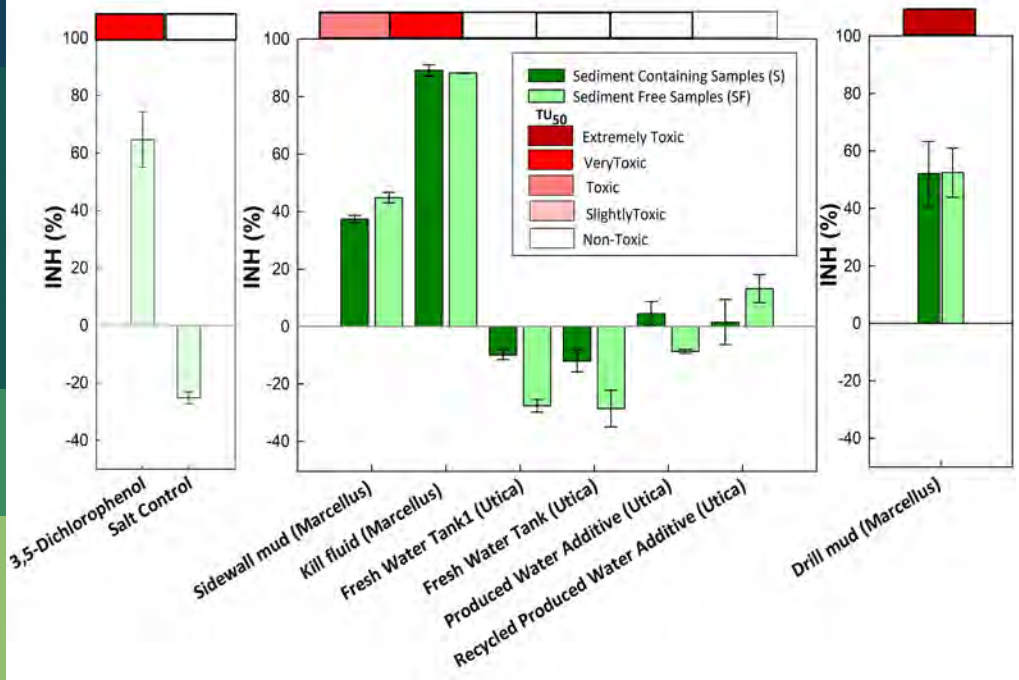
Utica-7
n= 8 FPW

Total number of input media and FPW samples: 42

Sample Analyzes

Aqueous chemistry parameters – Input media and FPW	Method
Benzene	SW8260
Toluene	SW8260
Ethylbenzene	SW8260
Total xylene	SW8260
m,p-xylene	SW8260
o-xylene	SW8260
MBAS	SW8260
O&G	SW8260
DOC	Combustion/NDIR
TDS	Hach
Fe2+	Hach: 1,10-phenanthroline

General toxicity in Input media

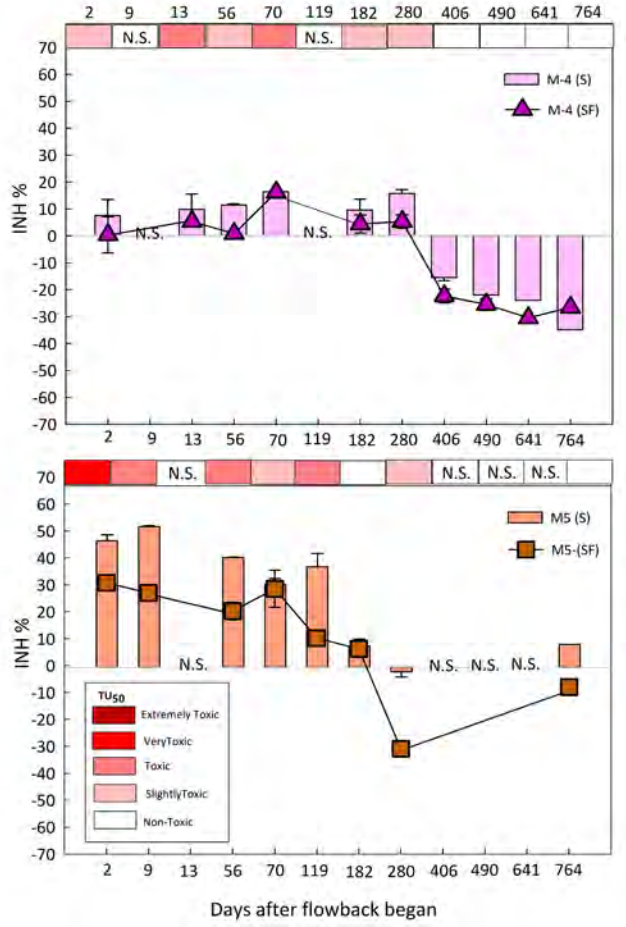


- Input media showing positive toxicity
- Average INH% of kill fluid and drill mud from Marcellus shale formation (Marcellus-4) was above that of the positive control sample (3,5 Dichlorophenol, INH%= 65%).
- The average INH% of examined freshwater tank inputs from Utica shale formation is negative.

General toxicity in Marcellus Shale Wells

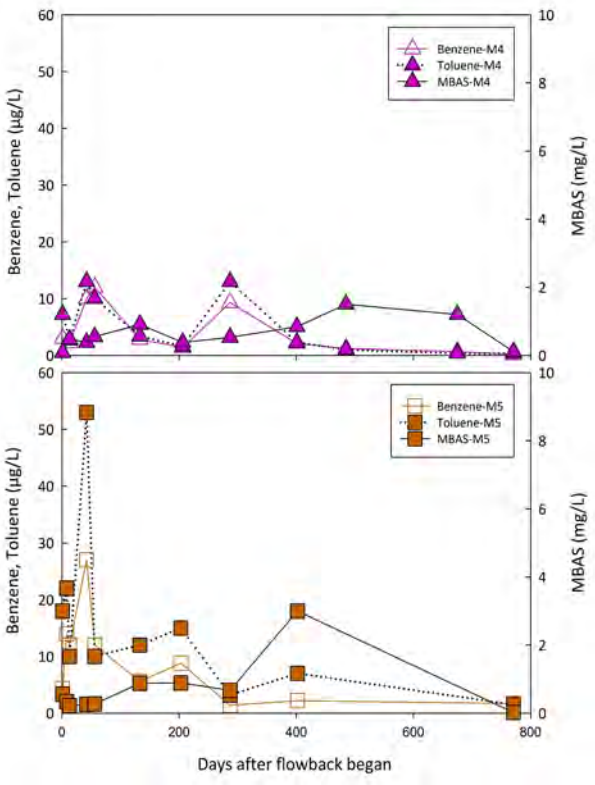
- The toxicity of early-stage flowback was higher than later time points for both filtered and unfiltered fractions.

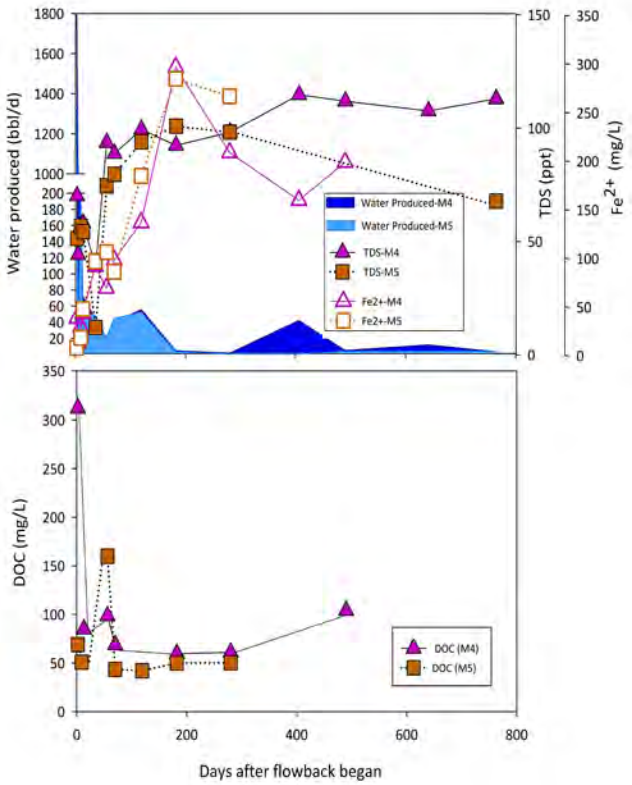
- Toxicity of FPW collected from two Marcellus Shale wells remained high six months after flowback began.



Aqueous Chemistry of Hydraulic Fracturing

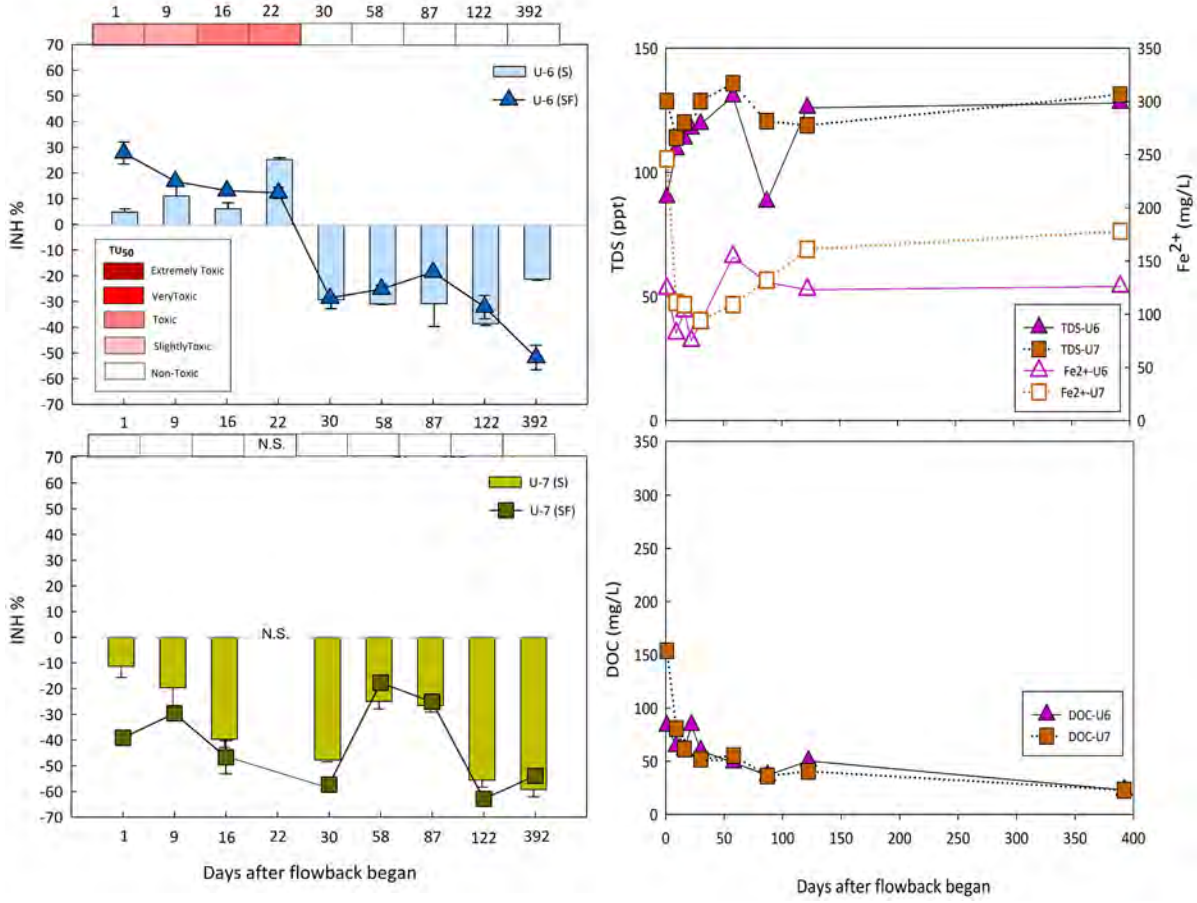
- There is a significant correlation between cytotoxicity level and benzene, toluene and MBAS concentrations ($p<0.05$).





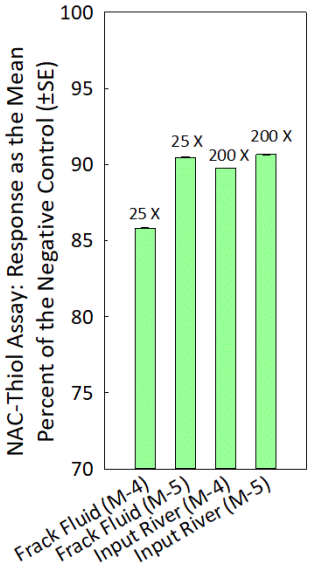
Bioluminescence Inhibition Results

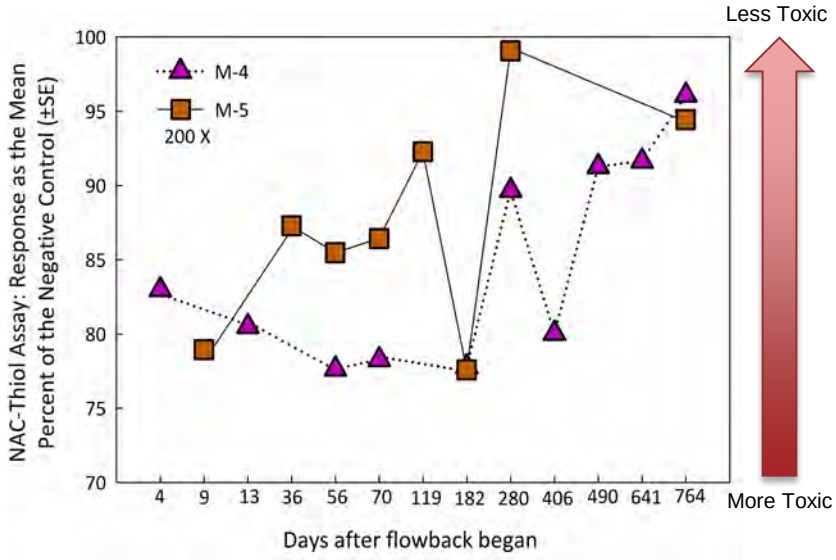
- The toxicity of early-stage flowback was higher than later time points for both filtered and unfiltered fractions in Utica-6 well.
- Toxicity of FPW from Utica Formation wells decreased substantially after one month.



NAC Thiol Reactivity in Marcellus Shale Wells

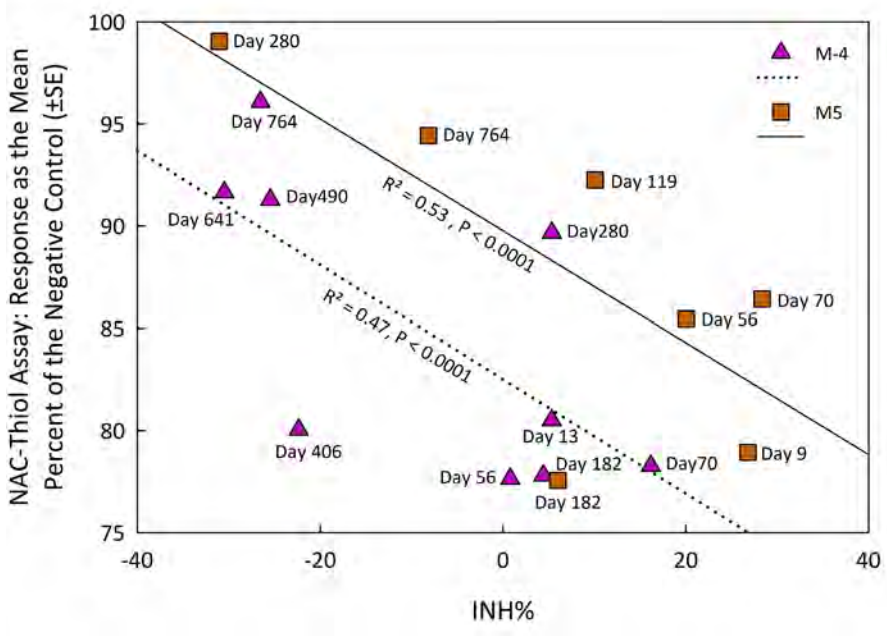
- The thiol reactivity of early-stage flowback was higher than that of fluids produced later for solid phase extraction (SPE) sample.
- The thiol reactivity of FPW in the Marcellus-4 well was higher than that in Marcellus-5.
- There is a significant correlation between thiol reactivity and benzene and toluene concentrations ($p<0.05$).





Comparison of NAC Thiol Reactivity and BLIA Results

- There is a significant correlation ($p<0.0001$) between the NAC-thiol reactivity and BLIA toxicity results of FPW samples in the Marcellus Shale natural-gas wells.



Conclusions

Hypothesis: There is a decrease in toxicity with time after hydraulic fracturing.

- Toxicity of FPW from four hydraulically fractured natural-gas wells Influenced by the length of time that wells have been producing FPW. The toxicity of early-stage flowback was higher than that of fluids produced later for both filtered and unfiltered fractions, indicating a decrease in toxicity as the natural-gas well matured.

Hypothesis: There is no difference in toxicity between replicate wells or shale formations.

- General toxicity was higher in Marcellus Shale wells as compared with Utica Formation; differences could be attributed to variations in source water for fracturing (recycled flowback versus freshwater), fracturing fluid composition, geogenic organic constituents, and shale geochemistry including salinity.

Conclusions

Hypothesis: Removal of sediments and associated hydrophobic organic matter and metals decrease the toxicity.

- The temporal variability in toxicity in the FPW-S and FPW-SF showed a similar trend, but there was a significant difference between the toxicity of the filtered and unfiltered fractions ($p<0.05$) in the Marcellus Shale natural-gas well (Marcellus-4).
- There was no significant difference between the toxicity of the filtered and unfiltered fractions in Marcellus Shale natural-gas well (Marcellus-5).
- Temporal variability in toxicity in the FPW-S and FPW-SF was not significant ($p>0.05$) in the Utica-Point Pleasant Formation (Utica-6 and Utica-7).

Conclusions

Hypothesis: There is no toxicity in the input media.

- High value of toxicity was detected for input media (kill fluid, drill mud, and sidewall mud). Input media showing positive toxicity, average INH% of kill fluid from Marcellus shale formation (Marcellus-4) was above that of the positive control sample (3,5-Dichlorophenol, INH%= 65%).

THANKS!

Any questions?

Mina Aghababaei
Ph.D. Student
Environmental Engineering
University of New Hampshire
Email: ma1127@wildcats.unh.edu